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Methods of the Ecotoxicological Evaluation of Chemicals

Photochemical Degradation in the Gas Phase

Volume 6:

OH Reaction Rate Constants and Tropospheric Lifetimes of Selected Environmental Chemicals

Report 1980 – 1983

Editors:

K.H. Becker, H.M. Biehl, P. Bruckmann, E.H. Fink, F. Führ, W. Klöpffer, R. Zellner, C. Zetzsch

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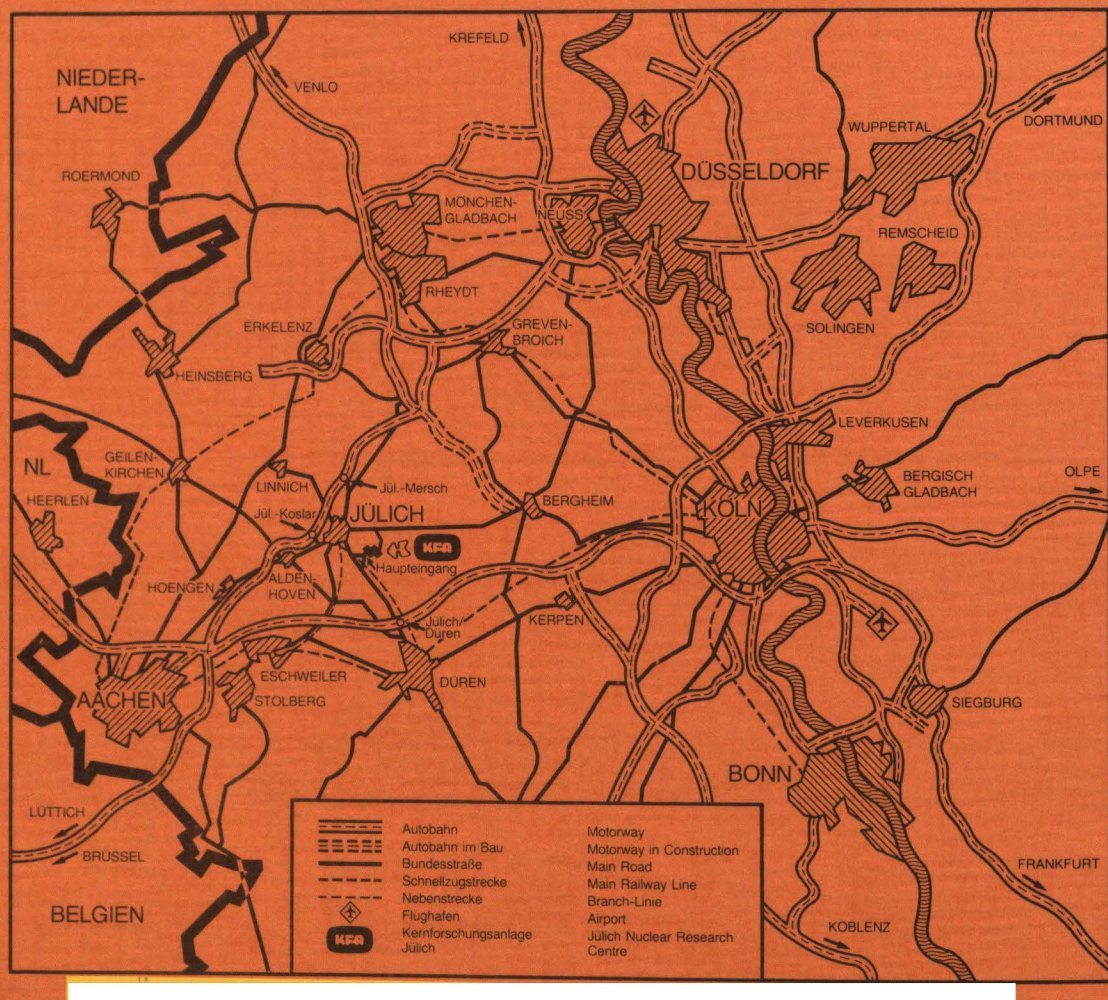

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1 Preface

More than a thousand chemical compounds are known to be emitted into the atmosphere from both natural and anthropogenic sources /1/. The awareness of environmental problems associated with these emissions has led the European Community and German legislation to establish testing procedures for the atmospheric behaviour of chemicals. The particular aim of such tests should be to determine the lifetime and degradation pathways of environmental chemicals in the troposphere.
The earth's atmosphere is a complex chemical system. The concentration levels of its trace constituents are regulated by the interaction of chemical processes, transport and mass exchange with hydro- and lithosphere. Regarding man-made emissions, transport is only a dilution phenomenon. The only relevant degradation occurs via chemical reactions.

Chemical degradation in the atmosphere is a result of direct and indirect photochemical reactions. It is now a well established fact that, among the homogenous gas phase processes, reactions initiated by the hydroxyl (OH) radical provide the most important degradation routes. This is based on the OH reactivity, as expressed by the rate coefficient k_{OH}, and the atmospheric OH concentration level (see section 5).

The present work contains the results of a comprehensive determination of the OH reactivity performed in different laboratories in Germany. It is part of the research project "Methods of the Ecotoxicological Evaluation of Chemicals. Photochemical Degradation in the Gas Phase", initiated jointly by Bundesministerium des Innern (BMI) and Bundesministerium für Forschung und Technologie (BMFT) and performed in accordance with the aims laid out by these agencies /2/. The work was sponsored by BMFT and in part by Verband der Chemischen Industrie (VCI).
Although this work concentrates on one reactive species only, namely OH, it should also be mentioned that there are numerous other processes, both homogenous and heterogenous, that contribute to the degradation of chemicals in the atmosphere, e.g. direct photochemical reactions, reactions with O_3 and HO_2 and heterogenous processes on surfaces of aerosols and soils. With few exceptions where direct photolysis (i.e. formaldehyde), HOO-reactions (i.e. formaldehyde) and O_3-reactions (i.e. higher olefins) become comparable

in rate to the removal by OH, the latter is always dominant. This is the inherent justification for the present work.

Due to the accepted importance of the OH reactions, a large body of rate data has been accumulated over the last 15 years. This is well documented in various reports and reviews /3-6/. However, the results so far available are limited in the number of compounds investigated and conditions applied. This is due to the difficulty to obtain rate data for species with low vapour pressure (i.e. hexachlorobenzene (HCB), DDT, DEHP (diethylhexylphthalate), pentachlorophenol (PCP), urea, polycyclic aromatic hydrocarbons) and for a broad range of atmospheric conditions. The latter is imposed by the fact that a number of OH reaction rates are dependent on total pressure and change in the presence of O_2. With the realization of previous achievements in OH gas kinetic studies and in accordance with the requirements of future testing procedures of chemicals, the purpose of research carried out within this project can be summarized as follows:

i to improve and extend existing kinetic methods and to develop standardized testing procedures

ii to test direct and indirect methods using a common set of reference chemicals

iii to meet experimental conditions that allow a direct transfer of laboratory results to the atmospheric environment

The present report is arranged according to these topics, beginning with a detailed description of the different experimental techniques applied within this project; in the following the results obtained from both, absolute and relative techniques are summarized in tabular form. Morevover, the use of laboratory kinetic data in order to estimate lifetimes of chemicals in the atmospheric environment and problems associated with this procedure will be discussed in the last section.

As will be seen from the tables not all of the chemicals contained in the list of reference chemicals /2/ selected according to a wide range of physicochemical properties and production figures of chemical industry have yet been studied. Among these, the low vapour pressure compounds. However, it appears that due to the experimental facilities and techniques available this is not a principal limitation. Their study requires time consuming experiments which will hopefully be undertaken in the near future. An extension of the present report to include such compounds is planned.

2 Experimental Methods to Determine OH Reaction Rate Coefficients

The methods applied can be divided into absolute and relative methods. In the absolute methods the time profile of the OH concentration is monitored in the presence of an excess of a single added chemical. Absolute rate constants are determined from the decay rate of OH and from the known (absolute) concentrations of the chemicals.
In the relative methods, the time profiles of at least two chemicals (in relative concentration) are monitored simultaneously in the presence of a steady state concentration of OH. Rate coefficients are determined relative to the known rate constant of the reference compound.

2.1 Absolute Methods

Method A:
Flash photolysis/resonance fluorescence
(Zetzsch et al., Bochum):

The principle of the method is shown in figure A . The optical geometry of OH-producing, OH-exciting and OH-detecting light paths at right angles applies to methods A to C. In method A,OH radicals are produced by pulsed vacuum UV photolysis ($\lambda > 105$ nm) of H_2O in the presence of the chemical and inert gas (Ar or He) using a spark discharge (E = 2J) in N_2 at atmospheric pressure as light source. In the reaction vessel, total pressures of Ar or He ranging from 5-1000 mbar can be used. The resonance fluorescence is excited continuously by light from a microwave discharge of H_2O in Ar at 2 mbar. OH radicals are detected by observing the time resolved resonance fluorescence OH ($A^2\Sigma^+ - X^2\Pi$) using photon counting and signal averaging (usually 100 subsequent decays) by multichannel scaling. Typical time resolution is 1 ms, OH can be observed from 0.1-3000 ms after the producing flash. Initial concentrations of OH are of the order of $5 \cdot 10^{10}$ cm^{-3} and the detection limit $< 10^8$ cm^{-3}. The concentrations of the chemicals are controlled by a gas saturation method. These reactants are present in large excess, and absolute rate constants of the reactions of OH with the chemicals are determined from pseudo-first order decays of OH in the presence of the chemical. Gaseous, liquid and solid chemicals with vapour pressures $> 10^{-2}$ hPa have been investigated.

At present the estimated lower bound of vapour pressure, P, and reactivity, k_{OH}, of a compound to be tested is $P \cdot k_{OH} > 1 \cdot 10^{-16}$ hPa $\cdot$ $cm^3 s^{-1}$ /7/.

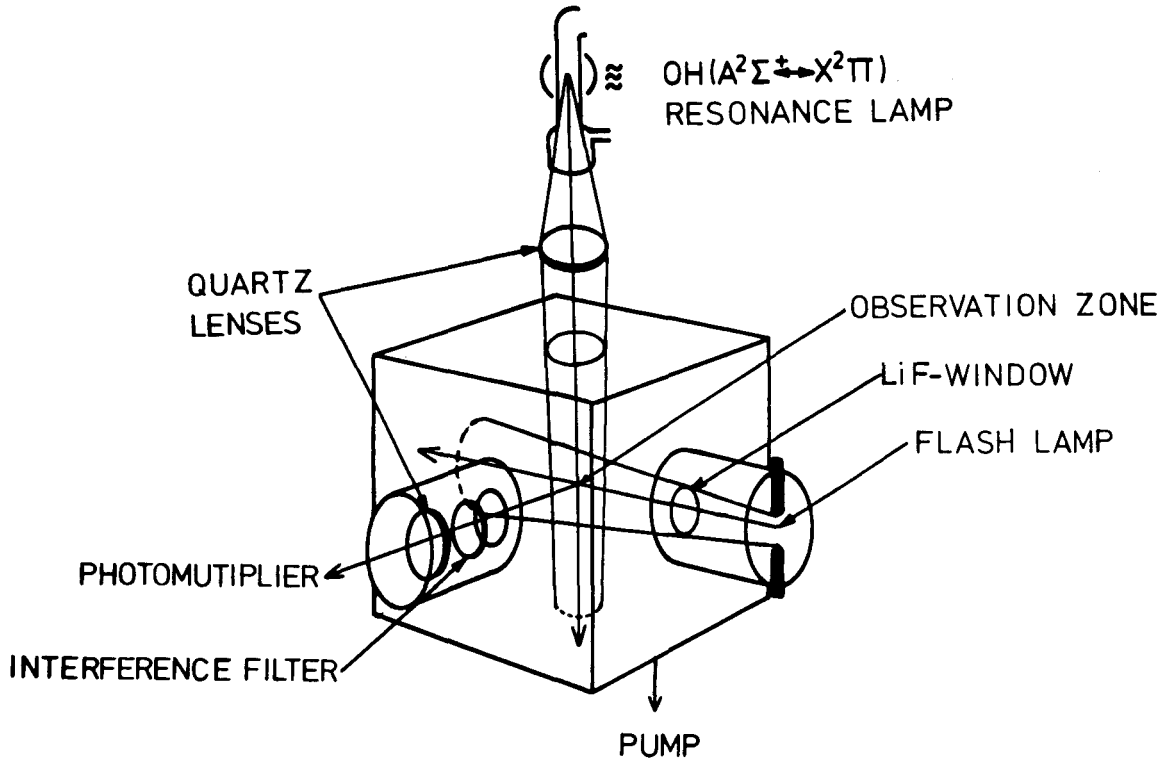

Fig. A: Schematic representation of flash photolysis/ resonance fluorescence system.

Method B:

Laser photolysis/resonance fluorescence

(Zellner et al., Göttingen):

In this technique an excimer laser is used as a short pulse monochromatic light source for the photolytic generation of OH radicals. Due to the availability of various UV laser lines (notably 193, 248, 351 nm), the photolytic precursor of OH (e.g. H_2O_2, HNO_3, O_3/H_2O, HNO_2) can be chosen as to avoid as much as possible unwanted photolysis or photoexcitation of the stable reagent. Unlike the conventional flash photolysis, the number density of OH-radicals generated in laser photolysis can easily be estimated from the relation

$$[OH]_o = N \cdot [precursor] \cdot \sigma_{precursor} \cdot \phi_{OH}$$

where N is the number of incident photons/cm^2 [ ] and σ are the concentration and absorption coefficient of the precursor and ϕ_{OH} is the OH quantum yield. For typical conditions of our experiments with HNO_3 as a source we estimate $[OH]_0 \sim 4 \times 10^{11}$ cm^{-3}. This is low enough to exclude any interference of our rate measurements with secondary reactions.

The time dependence of OH is followed using conventional A - X resonance fluorescence excited by a microwave discharge of H_2O in Ar. Resonantly scattered photons are collected by quartz optics via a 306 nm interference filter, focussed on a photomultiplier and fed into a signal averager.

The reaction cell can be thermostated between 250-650 K. The heating facility in particular is included to allow rate measurements for OH reactions with low volatile compounds. Total pressures in the system can be varied between 2-300 hPa of Ar. Measurements in air are precluded due to strong quenching of the OH fluorescence intensity (Fig. B) /8/.

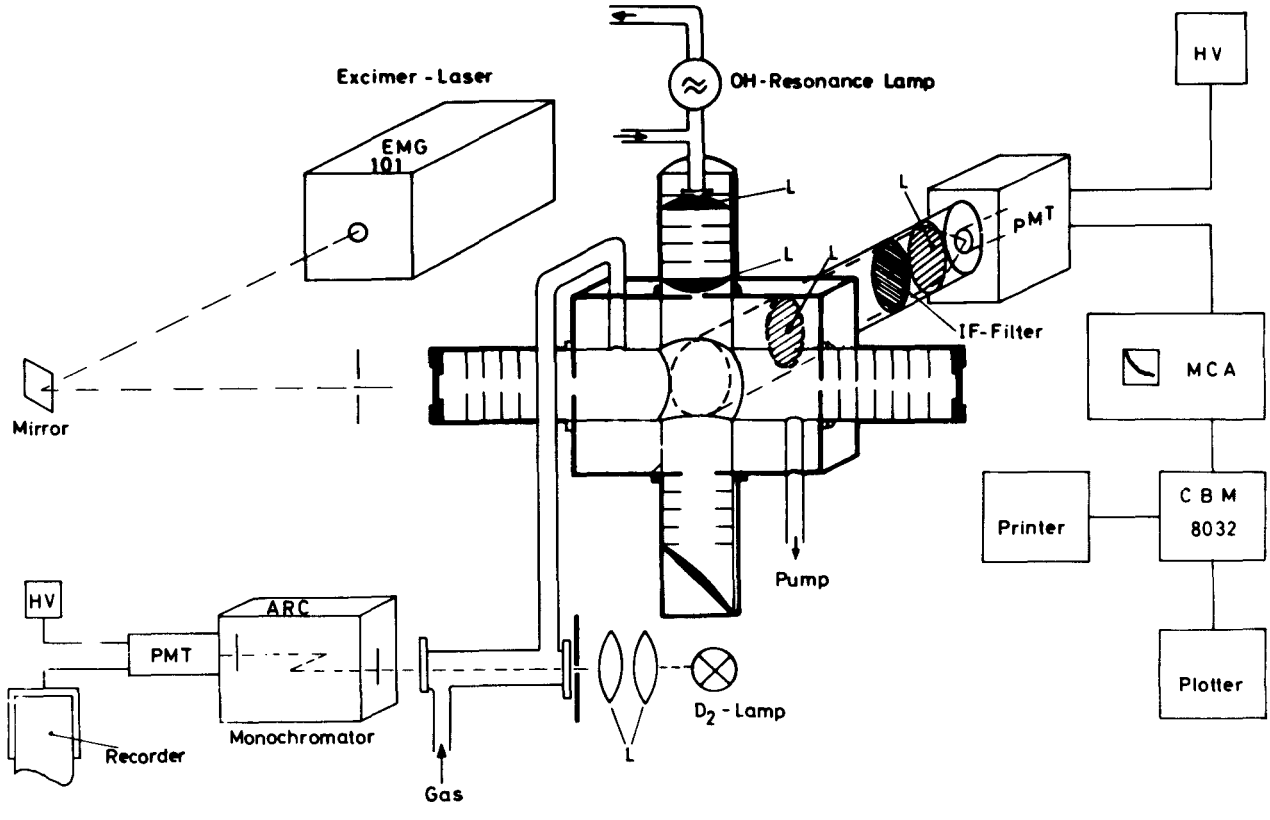

Fig. B: Schematic representation of excimer laser photolysis/ resonance fluorescence system

Method C:
Laser-Photolysis/ Laser Induced Fluorescence
(Fink et al., Wuppertal):

Laser induced fluorescence measurements with a high energy pulsed dye laser offer a means to follow low concentrations of OH radicals at total pressures up to 1 atm and in the presence of strongly quenching diluent gases like O_2 or H_2O. This technique thus allows the study of OH reactions under tropospheric conditions.
As in method B, pulse photolysis of H_2O_2 or HNO_3 with the ArF (193 nm) or KrF (248 nm) emission of an excimer laser (LAMBDA PHYSIK Model EMG 102) is used to generate OH radicals at concentrations of 10^9-10^{12} cm^{-3}. To follow their reaction, the OH-radicals are excited to the $A^2\Sigma^+$, v' = 1 state by absorption of a frequency doubled dye laser pulse (QUANTEL Model YG 481/TDL III) in the (1.0) band of the $A^2\Sigma^+ \leftarrow X^2\Pi$ transition at 282 nm. The fluorescence intensity of the (0,0) band at 309 nm is taken as a measure of the radical's ground state concentration. At high air pressure Raman scattering of the exciting laser light by O_2 and N_2 leads to first Stokes bands at 295 nm and 302 nm, respectively. To discriminate the OH fluorescence from these Raman bands and to suppress the intense background emission due to Rayleigh scattering of the laser light, a double monochromator (SPEX Doublemate) with a bandwidth of 3-5 nm is used to isolate the OH fluorescence at 309 nm. The fluorescence light pulses are measured with a photomultiplier and averaged in a boxcar integrator. By shifting the time delay between the excimer laser pulse generating the OH radicals and the fluorescence measurement with the dye laser, the exponential decay of the OH due to reaction with an excess of reactant can be followed on typical time scales of 10 µs to 10 ms.
The experiments are performed in a temperature controlled stainless steel fluorescence cell. To reduce impurity effects and to avoid a piling up of reaction products, a slow flow of carrier gas (argon or synthetic air) containing suitable concentrations of the OH parent compound and of the reactant under study is continuously passed through the fluorescence cell /9/. A schematic view of the experimental set up is shown in Fig. C.

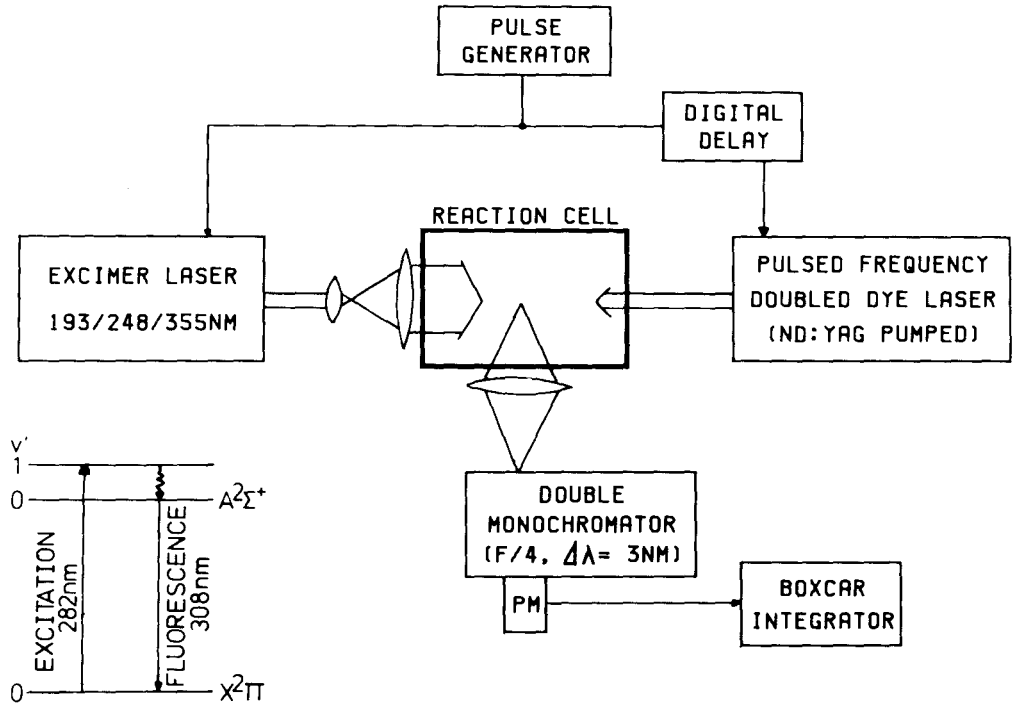

Fig. C: Schematic diagram of the excimer laser photolysis/ dye laser fluorescence experiment

Method D:

Laser photolysis/ laser absorption

(Zetzsch et al., Hannover):

OH radicals are produced by excimer laser photolysis of H_2O at 193nm or of H_2O_2 at 248 nm in the presence of the chemical and a buffer gas (e.g. air). Figure D gives an outline of the experimental arrangement. The decay profile of OH is monitored by long path UV absorption in a 150 m light path, folded into a 1 m cell, using an externally frequency doubled ring dye laser. The laser delivers 1 mW at 308 nm with a bandwidth < 1 MHz which is much smaller than the Doppler-width of OH at room temperature. A differential absorption system is capable of a detection limit of $< 10^7$ OH radicals per cm^3 at 40 µs time resolution and 50 decays averaged. Low initial concentrations of OH around 10^9 cm^{-3} are used in order to avoid interfering secondary radical reactions. In contrast to laser and classical resonance fluorescence methods, the method is not subject to a significant loss of sensitivity at atmospheric pressure in presence of quenching gases.

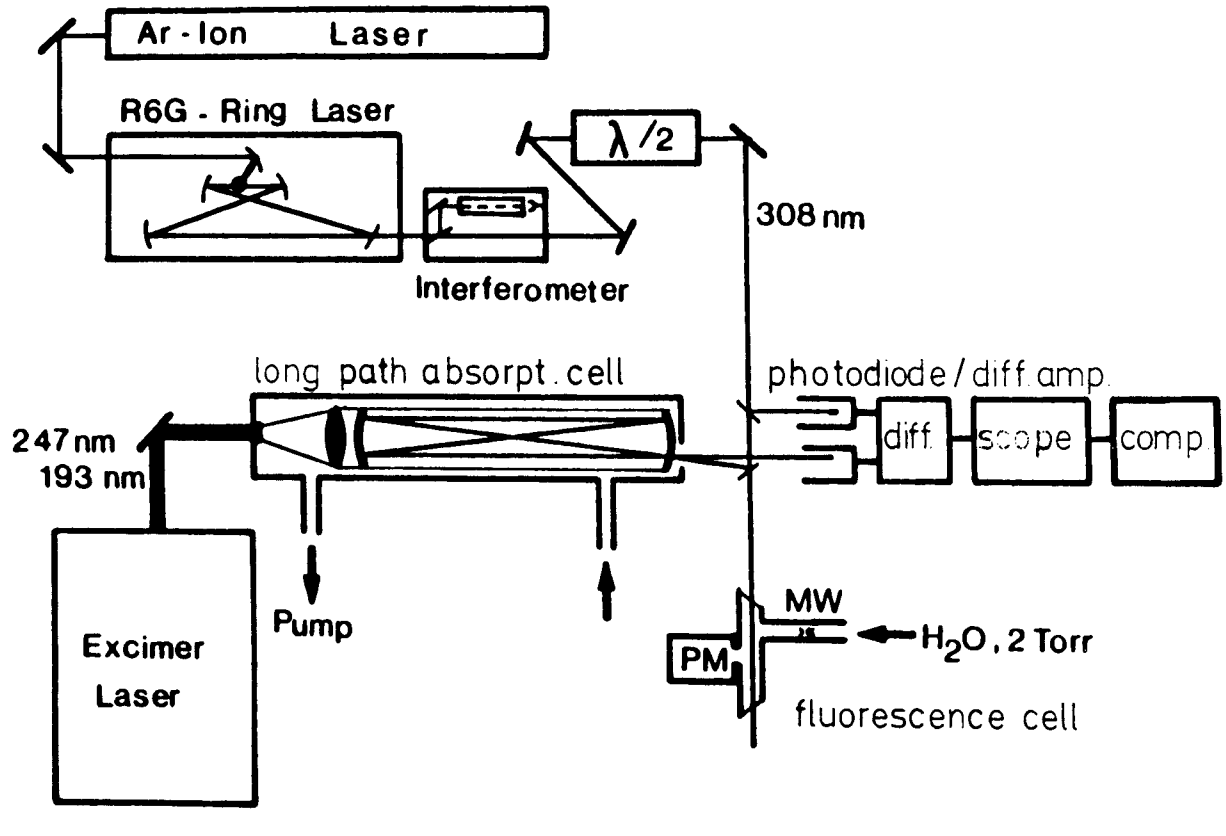

Figure D : Outline of the laser photolysis/ laser absorption method, showing the detection by the Ar-ion laser, the ring dye laser, the reference interferometer, the external frequency doubling, the long path absorption cell with the differential absorption.

2.2 Relative Methods

Method E:

Smog Chamber
(Becker et al., Wuppertal):

OH rate constants are determined by relative rate methods using three environmental chambers (420, 40 and 20 l) from Duran glass surrounded by photolysis lamps. Both photolytical and nonphotolytical ("dark") methods are applied for the generation of OH radicals. Reaction mixtures are analyzed by gas chromatography and Fourier-Transform infrared (FTIR) absorption spectroscopy using a built-in White mirror system with an optical path length of ~ 50 m (420 l chamber).
OH radicals are generated by the following methods:

(a) Thermal decomposition of HO_2NO_2 in the presence of NO (dark source)
(b) Photolysis of CH_3ONO in the presence of O_2 and NO
(c) Photolysis of HONO
(d) Photolysis of NO_x in the presence of a hydrocarbon and air

Rate constants determined using the latter method (d) are not included in the data sheets because of the uncertainty in the mechanism of OH formation in such reaction systems and possible complications due to secondary reactions of active species formed by the photolysis of NO_2.

Two compounds R_1 and R_2 are added to one of these OH sources, and the concentrations R_1 and R_2 are measured as a function of time. Evaluation of the rate data for the reactions

$$R_1 + OH \longrightarrow \text{products} \qquad k_1$$

$$R_2 + OH \longrightarrow \text{products} \qquad k_2$$

proceeds according to the equation

$$\frac{\log\left([R_1]_{t_1} / [R_1]_{t_2}\right)}{\log\left([R_2]_{t_1} / [R_2]_{t_2}\right)} = \frac{k_1}{k_2}$$

Chemicals are investigated in the presence of the reference substances R_2 = n-butane, n-hexane, ethene, propene, cis-2-butene, benzene, ethane, and propane.

Newer data from recent measurements have been incorporated in the evaluation of some of the rate constants and consequently small deviations may exist between the values reported here and those previously published.
The following experimental modifications are specified in the data sheets:

E1a: 420 l chamber, dark OH source
E1b: 420 l chamber, photolysis of CH_3ONO
E2a: 40 l chamber, dark OH source
E2b: 40 l chamber, photolysis of CH_3ONO
E2c: 40 l chamber, photolysis of HONO
E3b: 20 l chamber, photolysis of CH_3ONO

Ref. /11/

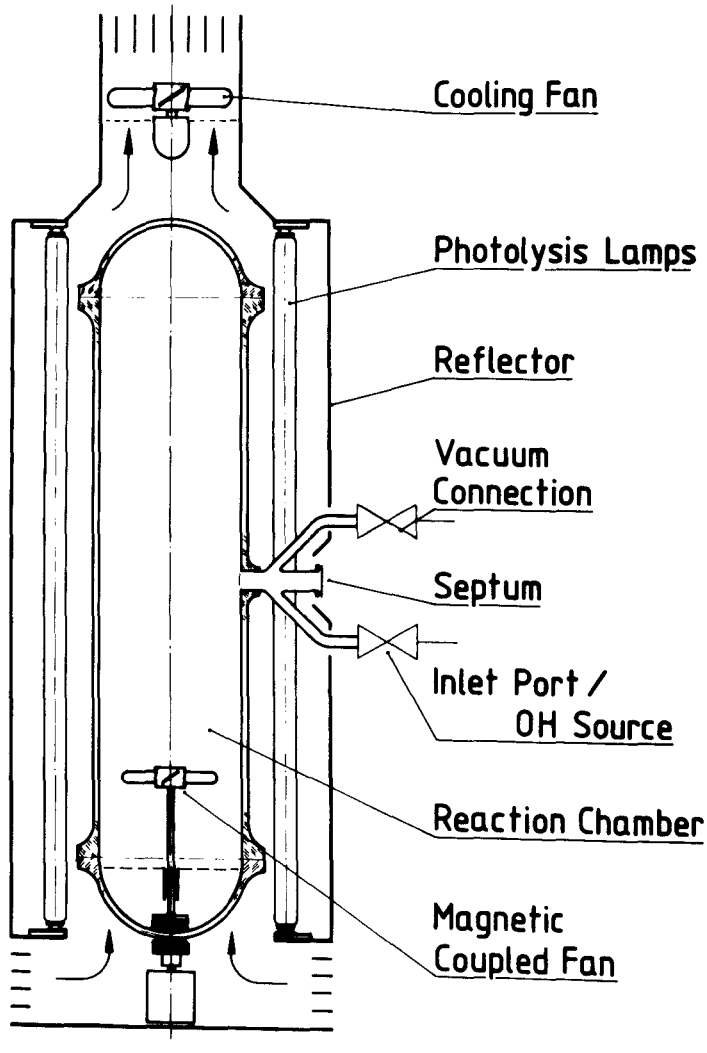

Fig. Ea: 40 l photoreactor for room temperature

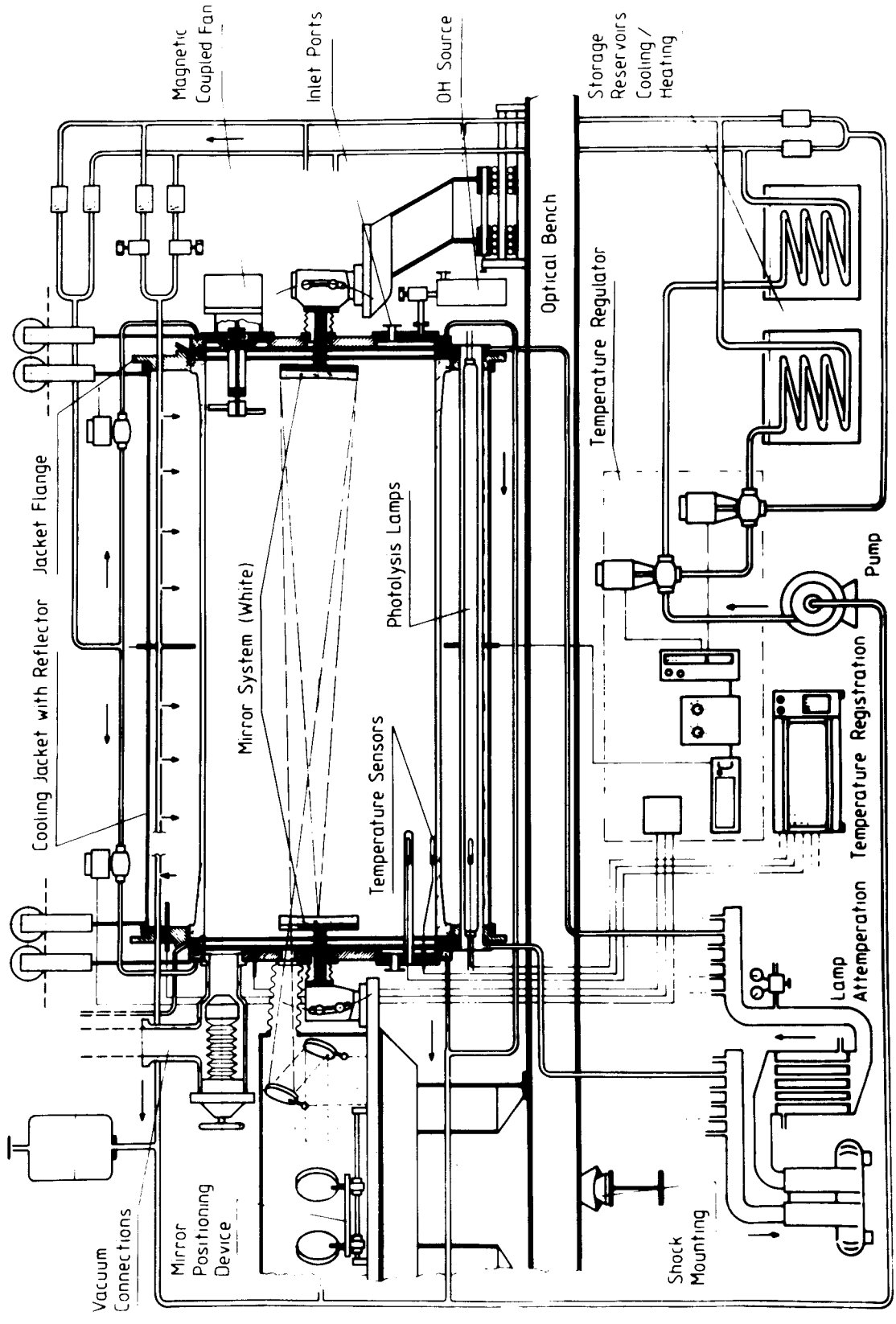

Figure Eb: 420 l photoreactor with FTIR analysis system

Method F:
(Medium size) smog chamber
(Klöpffer et al.):

A 450 liter chamber made of DURAN glass is used to produce photochemical smog. The UV radiation necessary to initiate and to sustain the chain reactions is secured by 28 UV-A lamps surrounding the cylindrical part of the reaction chamber. NO, NO_2 , O_3, p, T and relative humidity are monitored. The decrease of concentration of test substance and reference is measured in variable time intervalls using a suitable analytical method, mostly GC. The rate constant k_{OH} is derived relative to the known one of the reference compound. Typical initial concentrations of smog-forming compounds (NO, ethene) are in the range of 1 ppm, initiaL concentrations of test- and reference compounds are about 100 ppb.
Instead of using a classical photosmog as source of OH radicals, HNO_2 may be photolysed using the same irradiation conditions. HNO_2 is produced externally from solutions of $NaNO_2$ and sulfuric acid.
Solid substances are introduced into the reaction chamber by means of a special evaporator.

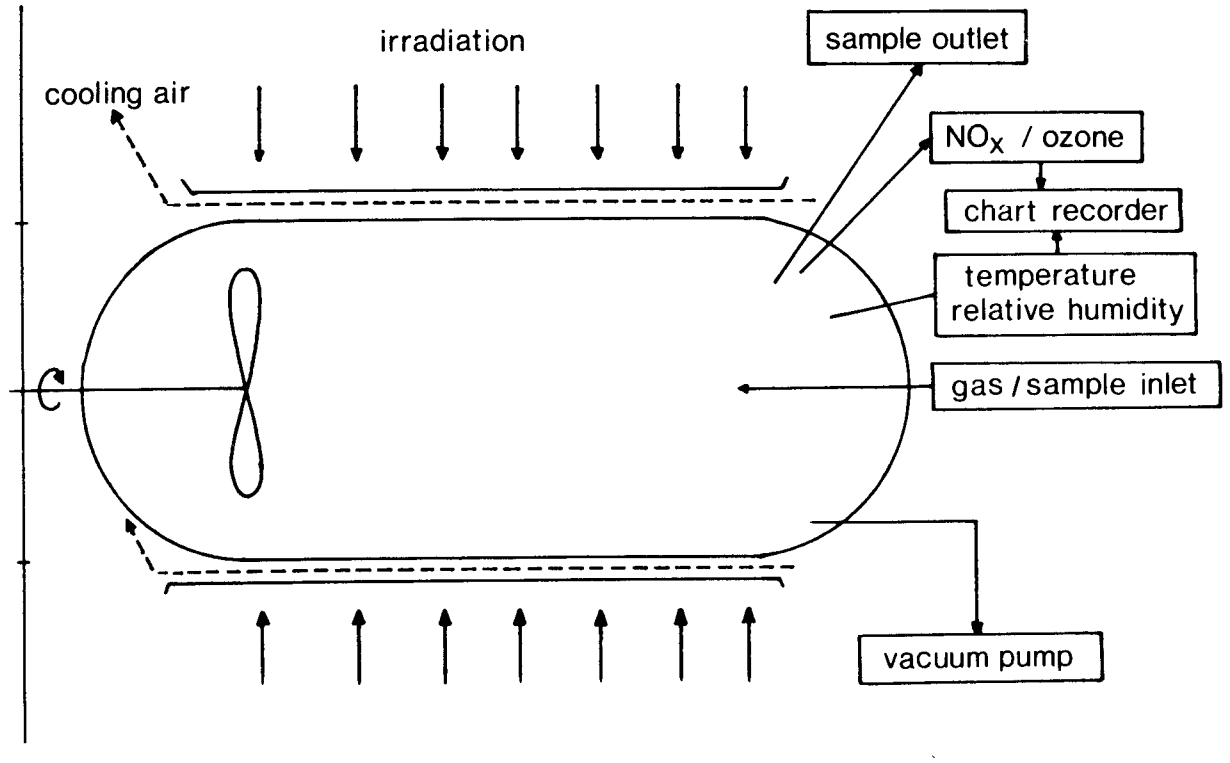

Figure F: Schematic diagram of the smog chamber at Battelle-Institut e.V., Frankfurt. Temperature and relative humidity are measured continually. On account of a large gas consumption of the devices NO_x and O_3 are measured only for short time intervals. In order to avoid contamination, a membrane pumpe is used for evacuation.

Method G:

Medium size smog chamber

(Bruckmann et al., Essen):

Rate constants relative to ethene (k_{OH} = 8,0 x 10^{-12} cm^3 s^{-1}) were obtained by irradiating hydrocarbon/NO_x-mixtures in purified air within a 520 liter allglass smog chamber at atmospheric pressure. The temperature during the runs was kept at 300 °K $\pm$ 1 K, the relative humidity ranged from 70% to 90%. The illumination system consisted of a 2.5 KW metal halogenide lamp (type HMI, Osram Co.), and a parabolic reflector, yielding an almost parallel light beam which passed through the chamber axially. The irradiation strength was measured by NO_2 photolysis and was typically in a range of 0.5-1.0 min^{-1}. Details of the chamber and the systems for dynamic dosage, air purification etc. have been described elsewhere /1/. NO_x and O_3 were measured by chemiluminescence. The decay of the organic compounds was followed by capillary gas chromatography /2/. As only sample sizes of less than 100 ml per hour were withdrawn, the dilution of the chamber content could be neglected. In a typical experiment, NO_x concentrations amounted to 300-1000 ppb with an initial NO/NO_2 ratio of 10:1, and the concentrations of the single organics were in the range of 10-50 ppb, thus guaranteeing a high enough surplus of NO to keep O_3 concentrations low /12/.

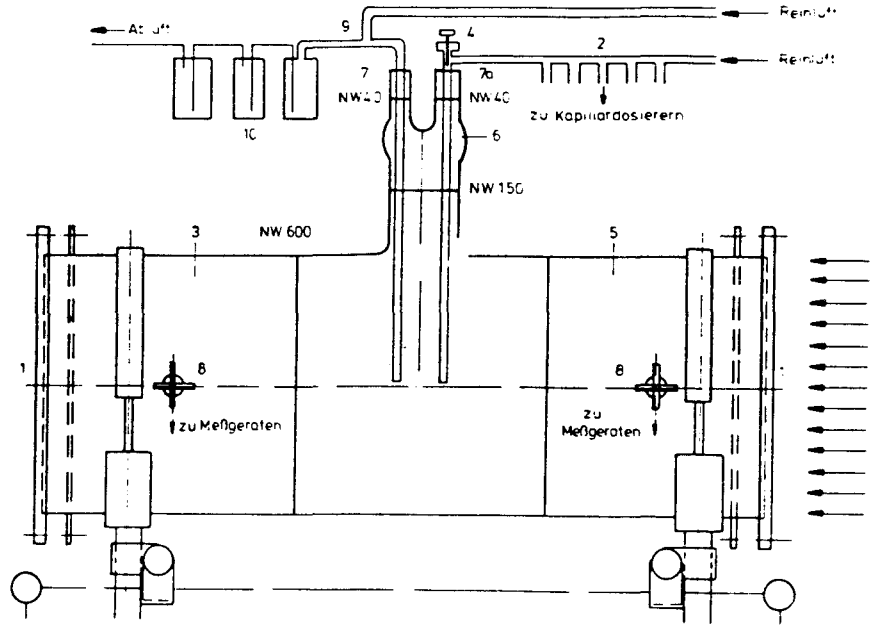

Fig. G: Smog chamber of method G, consisting of pyrex glass reactor, thermostating unit, solar simulator, dynamic dosage system and measurement instruments

Method H:

Aerosol-smog chamber

(Fraunhofer-Gesellschaft):

A 2.4 m^3 chamber designed for long residence times of aerosols is used to produce photochemical smog by irradiation of NO_x. An outline of the setup and the computer control is given in figure H . The chamber is a vertical cylinder (diameter: 1 m, height: 3 m) made of pyrex glass. A bunch of 7 high pressure lamps (Osram HMI, 1200 W) irradiates the chamber from the top using 3 mm pyrex and a 3 cm water layer as filter. The chamber is thermostated at room temperature, the intensity of the simulated solar irradiation (in terms of NO_2 photolysis rate) is $k_{NO_2} = 1.15\ min^{-1}$. Initial concentrations of NO and NO_2 are typically 100 ppb each, NO is being added continuously during the runs in order to sustain a constant photochemical production of OH and to keep O_3 at a low level. Hydrocarbons are introduced at the 100 ppb level and are monitored using capillary GC down to the 1 ppb level. Smog chamber runs have been extended up to a time period of one week. Rate constants are given relative to n-Pentane, values are obtained from 6 runs consisting of 12 data points each /13/.

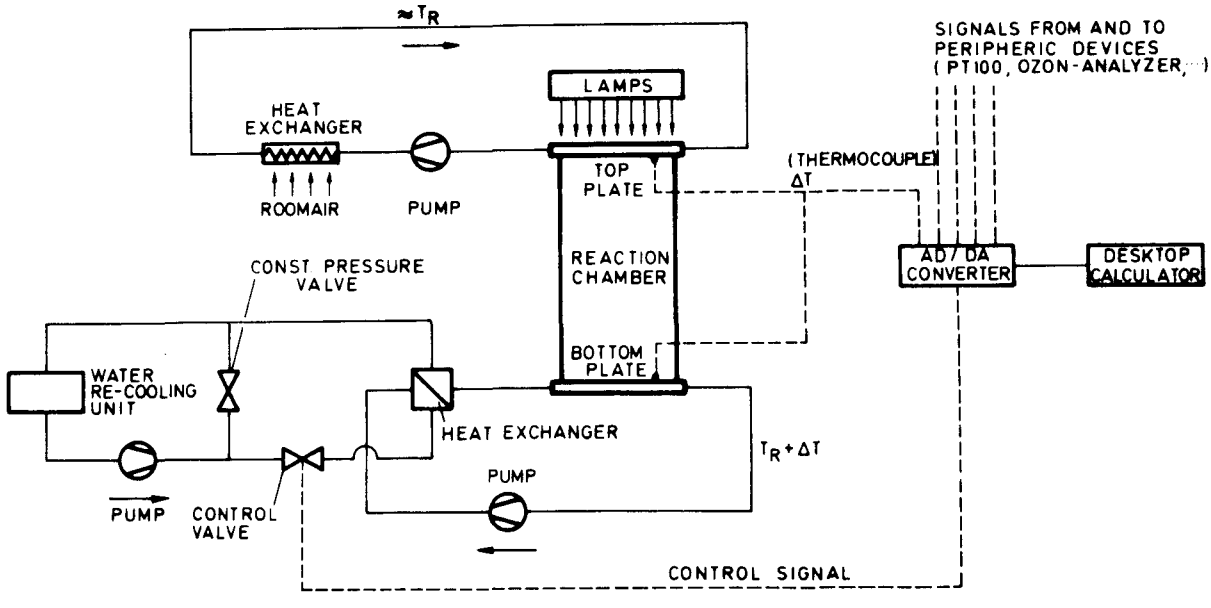

Figure H : Aerosol smog chamber and computer control diagram of the thermostating and the relevant experimental parameters.

Method I:

Rapid test in aqueous solution according to Walling (Klöpffer et al., Frankfurt):

In this method k_{OH} is measured in acidic, aqueous solution by means of H_2O_2/Fe^{++} (Fenton's reagent). A kinetic evaluation allows the determination of k_{OH} relative to the known value of the rate constant $OH + Fe^{++}$. The rate constants have to be extrapolated to the gas phase using a bilogarithmic relationship:

$$\log k_{OH} \text{ (gas phase)} = 0.906 \log k_{OH} \text{ (water)} + 1.112 \text{ l mol}^{-1}\text{s}^{-1}$$

This equation has been derived using the data of about 40 compounds for which both, water- and gas-phase k_{OH} values have been reported in the literature /14/.

3 Guide to Data Sheets

Rate coefficients reported in this work are given in molecular units, i.e. cm^3/s for reactions of second order and cm^6/s for third reactions. For more complete pressure dependent studies of a single reaction and whenever appropriate, the dependence of rate coefficients on total pressure is represented according to the reduced "fall-off" curves developed by Luther and Troe /15/

$$k(M) = \frac{k_o}{1 + k_o/k_\infty} \cdot F_c^{\,1/\left\{1 + \left[\log k_o/k_\infty\right]^2\right\}}$$

with the three parameters k_o, k_∞ and F_c, where k_o and k_∞ represented the rate coefficients in the limits of low and high pressure and F_c is the broadening factor in the center of the fall-off curve. Temperature dependencies of bimolecular reactions are given in Arrhenius from ($k(T) = A \exp(-E/RT)$) or modified Arrhenius form ($k(T) = A\,T^n \exp(-E/RT)$; $k(T) = \exp.(a + bT)$ /16/). M is a nature of the third body, $[M]$ is its total concentration.
All other quantities are quoted in SI unites.

Error limits quoted are different for the different experimental methods used. The following have been adapted:

Method:	Error limit and accuracy:
A	3σ (including students T)
B	absolute accuracy estimated from reproducibility and systematic errors
C	" "
D	3σ
E	1σ, for total error the estimated error of the reference reaction rate constant from the table below should be added
F	based on estimated accuracy of relative rate coefficient where specific
G	1σ determined from 7 independent measurements of the rate coefficients
H	Estimated from reproducibility where quoted
I	error limits not quoted

In the relative methods E, F, G and H the following rate coefficients and activation energies (for the temperature range 290-305 K) as taken from the literature have been used for the reference reactions R_i + OH —> products:

R_i	k_i (295 K, 1013 hPa synth. air) $[cm^3 s^{-1}]$	$E_a [kJ\ mol^{-1}]$
n-butane	$(2.5 \pm 0.3) \times 10^{-12}$	4.6
n-hexane	$(5.6 \pm 0.8) \times 10^{-12}$	4.2
ethene	$(8.0 \pm 1.0) \times 10^{-12}$	-3.2
propene	$(2.7 \pm 0.3) \times 10^{-11}$	-4.5
cis-2-butene	$(5.7 \pm 1.4) \times 10^{-12}$	-4.1
benzene	$(1.2 \pm 0.2) \times 10^{-12}$	-4.2
ethane	$(2.8 \pm 0.4) \times 10^{-13}$	5.1
propane	$(1.2 \pm 0.4) \times 10^{-12}$	5.6
n-pentane	$(4.1 \pm 0.6) \times 10^{-12}$	
toluene	$(6.1 \pm 0.9) \times 10^{-12}$	
mesitylene	5.5×10^{-11}	

4 DATA SHEETS

4.1 Alkanes

4.1.1 Methane

$$OH + CH_4 \longrightarrow CH_3 + H_2O$$

$k/cm^3\ s^{-1}$	T/K	p/hPa	Method	Comments
Absolute rate measurements:				
$(7.9 \pm 0.5) \times 10^{-15}$	298	13	B	M = He
Relative measurements:				
Relative solution data:				

4. 1.2 **Ethane**

$$OH + C_2H_6 \longrightarrow H_2O + C_2H_5$$

$k/cm^3\ s^{-1}$	T/K	p/hPa	Method	Comments
Absolute rate measurements:				
$(2.8 \pm 0.3)\ 10^{-13}$	298	13.3	B	M = He
$(2.2 \pm 0.3)\ 10^{-13}$	295	1013	C	M = synth. air
$(2.2 \pm 0.3)\ 10^{-13}$	295	1013	C	M = Argon
Relative measurements:				
$(3.1 \pm 0.3)\ 10^{-13}$	300	1000	E2b	M = synth. air R = n-butane

Relative solution data:

4.1.3 Propane

$$OH + C_3H_8 \longrightarrow H_2O + C_3H_7$$

$k/cm^3\ s^{-1}$	T/K	p/hPa	Method	Comments
Absolute rate measurements:				
$(1.3 \pm 0.3)\ 10^{-12}$	296	13.3	B	M = He
$(1.0 \pm 0.15)\ 10^{-12}$	295	1010	C	M = synth. air
Relative measurements:				
$(1.2 \pm 0.1)\ 10^{-12}$	295	1000	E1a	M = synth. air, R = ethene
$(1.2 \pm 0.1)\ 10^{-12}$	300	1000	E2b	M = synth. air, R = ethene
$(1.2 \pm 0.5)\ 10^{-12}$	300	1004	G	M = synt. air, R = ethene
Relative solution data:				

4. 1.4 n-butane

$$OH + C_4H_{10} \longrightarrow H_2O + C_4H_9$$

$k/cm^3\ s^{-1}$	T/K	p/hPa	Method	Comments
Absolute rate measurements:				
$(2.5 \pm 0.5)\ 10^{-12}$	296	13.3	B	M = He
$(2.3 \pm 0.3)\ 10^{-12}$	295	1013	C	M = synth. air
Relative measurements:				
$(2.53 \pm 0.20)\ 10^{-12}$	300	1000	H	M = synth. air, R = n-pentane
$(2.4 \pm 0.3)\ 10^{-12}$	300	1004	G	M = synth. air, R = ethene
Relative solution data:				

4. 1.5 iso-butane

$$OH + C_4H_{10} \longrightarrow H_2O + C_4H_9$$

$k/cm^3\ s^{-1}$	T/K	p/hPa	Method	Comments
Absolute rate measurements:				
$(2.3 \pm 0.5)\ 10^{-12}$	297	13.3	B	M = He
$(1.9 \pm 0.25)10^{-12}$	295	1013 ± 15	C	M = synth. air
Relative measurements:				
$(2.3 \pm 0.2)\ 10^{-12}$	300	986	E2b	M = synth. air, R = n-butane
$(2.0 \pm 0.3)\ 10^{-12}$	300	1004	G	M = synth. air, R = ethene
$(2.61 \pm 0.16)\ 10^{-12}$	300	1000	H	M = synth. air, R = n-pentane
Relative solution data:				

4. 1.6 n-pentane

$$C_5H_{12} + OH \longrightarrow H_2O + C_5H_{11}$$

$k/cm^3\ s^{-1}$	T/K	p/hPa	Method	Comments
Absolute rate measurements:				
$(3.9 \pm 0.8)\ 10^{-12}$	298	13.3	B	M = He
Relative measurements:				
$(3.8 \pm 0.4)\ 10^{-12}$	295	1000	E1a	M = synth. air, R = etnene
$(4.3 \pm 0.4)\ 10^{-12}$	300	986	E2b	M = synth. air, R = n-butane
$(5.7 \pm 0.9)\ 10^{-12}$	300	1004	G	M = synth. air, R = ethene
Relative solution data:				

4. 1.7 Isopentane

$$OH + C_5H_{12} \longrightarrow H_2O + C_5H_{11}$$

$k/cm^3\ s^{-1}$	T/K	p/hPa	Method	Comments
Absolute rate measurements:				
Relative measurements:				
$(4.0 \pm 0.4)\ 10^{-12}$	300	986	E2b	M = synth. air, R = n-butane
$(4.1 \pm 0.4)\ 10^{-12}$	300	1004	G	M = synth. air, R = ethene
$(4.08 \pm 0.07)\ 10^{-12}$	300	1000	H	M = synth. air, R = n-pentane
Relative solution data:				

4. 1.8 n-hexane

$$OH + C_6H_{14} \longrightarrow H_2O + C_6H_{13}$$

$k/cm^3\ s^{-1}$	T/K	p/hPa	Method	Comments
Relative Measurements:				
$(5.5 \pm 0.6)\ 10^{-12}$	295	1000	E1a	M = synth. air, R = ethene
$(5.7 \pm 0.6)\ 10^{-12}$	300	1000	E2b	M = synth. air, R = n-butane
$6.8\ 10^{-12}$	300	1050	F	M = synth. air, R = toluene
$(6.9 \pm 1.3)\ 10^{-12}$	300	1004	G	M = synth. air, R = ethene
$(5.42 \pm 0.10)\ 10^{-12}$	300	1000	H	M = synth. air, R = n-pentane

Relative solution data:

4. 1.9 3-methylpentane

$$OH + C_6H_{14} \longrightarrow H_2O + C_6H_{13}$$

$k/cm^3\ s^{-1}$	T/K	p/hPa	Method	Comments
Absolute rate measurements:				
Relative measurements:				
$(5.5 \pm 0.07)\ 10^{-12}$	300	1000	H	M = synth. air, R = n-pentane
Relative solution data:				

4. 1.10 2-methylpentane

$$OH + C_6H_{14} \longrightarrow H_2O + C_6H_{13}$$

$k/cm^3\ s^{-1}$	T/K	p/hPa	Method	Comments
Absolute rate measurements:				
Relative measurements:				
$(6.2 \pm 0.5)\ 10^{-12}$	300	1004	G	M = synth. air, R = ethene
Relative solution data:				

4.1.11 Cyclohexane

$$OH + C_6H_{12} \longrightarrow H_2O + C_6H_{11}$$

$k/cm^3\ s^{-1}$	T/K	p/hPa	Method	Comments
Absolute rate measurements:				
$(6.7 \pm 1.3)\ 10^{-12}$	295	13.3	B	M = He
Relative measurements:				
$(7.4 \pm 0.7)\ 10^{-12}$	300	1000	E2b	M = synth. air, R = n-butane
Relative solution data:				

4. 1.12 n-heptane

$$OH + C_7H_{15} \longrightarrow H_2O + C_7H_{14}$$

$k/cm^3\ s^{-1}$	T/K	p/hPa	Method	Comments
Relative measurements:				
$8.5 \quad 10^{-12}$	296-305	$1.05\ 10^3$	F	M = synth. air, R = toluene
$(8.6 \pm 0.6)\ 10^{-12}$	300	1004	G	M = synth. air, R = ethene
$(7.46 \pm 0.08)\ 10^{-12}$	300	1000	H	M = synth. air, R = n-pentane

Relative solution data:

4.1.13 n-octane

$$OH + C_8H_{18} \longrightarrow H_2O + C_8H_{17}$$

$k/cm^3\ s^{-1}$	T/K	p/hPa	Method	Comments
Absolute rate measurements:				
Relative measurements:				
$(8.68 \pm 0.15)\ 10^{-12}$	300	1000	H	M = synth. air, R = ethene
Relative solution data:				

4. 1.14 2,2,4-trimethylpentane

$$OH + C_8H_{18} \longrightarrow H_2O + C_8H_{17}$$

$k/cm^3\ s^{-1}$	T/K	p/hPa	Method	Comments
Absolute rate measurements:				
Relative measurements:				
$(4.2 \pm 1)\ 10^{-12}$	300	1000	G	M = synth. air, R = ethene
Relative solution data:				

4.1.15 n-nonane

$$OH + C_9H_{20} \longrightarrow H_2O + C_9H_{19}$$

$k/cm^3\ s^{-1}$	T/K	p/hPa	Method	Comments
Absolute rate measurements:				
Relative measurements:				
$(9.38 \pm 0.07)\ 10^{-12}$	300	1000	H	M = synth. air, R = n-pentane
Relative solution data:				

4.1.16 undecane

$$OH + C_{11}H_{24} \longrightarrow H_2O + C_{11}H_{23}$$

$k/cm^3\ s^{-1}$	T/K	p/hPa	Method	Comments
Absolute rate measurements:				
Relative measurements:				
$(13.8 \pm 0.8)\ 10^{-12}$	300	1000	H	M = synth. air, R = n-pentane
Relative solution data:				

4. 1.17 dodecane

$$OH + C_{12}H_{26} \longrightarrow H_2O + C_{12}H_{25}$$

$k/cm^3\ s^{-1}$	T/K	p/hPa	Method	Comments
Absolute rate measurements:				
Relative measurements:				
$(14.2 \pm 1.0)\ 10^{-12}$	300	1000	H	M = synth. air, R = n-pentane
Relative solution data:				

4.2 Alkenes / Alkynes

4.2.1 Ethene

$$OH + C_2H_4 \longrightarrow \text{products}$$

$k/cm^3\ s^{-1}$	T/K	p/hPa	Method	Comments
Absolute rate measurements:				
$(2.2 \pm 0.5)\ 10^{-12}$	296	4	B	
$(5.6 \pm 1.0)\ 10^{-12}$	296	13.3		M = Ar, a)
$(7.6 \pm 1.4)\ 10^{-12}$	297	42.3		
$(6.3 \pm 1.4)\ 10^{-12}$	295	79.3		
$(7.3 \pm 1.5)\ 10^{-12}$	296	128.7		
$(5.5 \pm 1.1)\ 10^{-12}$	335	45.8		
$(3.0 \pm 0.7)\ 10^{-12}$	378	47.8		
$(2.0 \pm 0.3)\ 10^{-12}$	437	41.4		
$(1.1 \pm 0.1)\ 10^{-12}$	521	38.3		
$(1.3 \pm 0.1)\ 10^{-12}$	524	40.7		
$(1.7 \pm 0.3)\ 10^{-12}$	525	52.7		
$(2.1 \pm 0.4)\ 10^{-12}$	524	67.3		
$(2.0 \pm 0.3)\ 10^{-12}$	524	78.2		
$(2.3 \pm 0.5)\ 10^{-12}$	522	123.6		
$(7.3 \pm 1.0)\ 10^{-12}$	295	1013	C	M = synth. air

a) Pressure dependence interpreted in terms of a "fall-off" curve calculated from symmetrical Kassel integrals. $k_0[Ar] = (5.5 \pm 2.5)\ 10^{-29}\ cm^6/s$ and $k_\infty = (8.8 \pm 1.6)\ 10^{-12}\ cm^3/s$, $F_c = 0.8$ /17/

4. 2.1 (continued)

$k/cm^3\ s^{-1}$	T/K	p/hPa	Method	Comments
Relative measurements:				
$(8.06 \pm 0.75)\ 10^{-12}$	295	1004	E1a	M = synth. air, a) R = n-hexane
$(7.70 \pm 0.35)\ 10^{-12}$		534		
$(7.68 \pm 0.56)\ 10^{-12}$		272		
$(7.30 \pm 0.39)\ 10^{-12}$		133		
$(6.96 \pm 0.28)\ 10^{-12}$		67		
$(5.90 \pm 0.16)\ 10^{-12}$		27		
$(4.97 \pm 0.13)\ 10^{-12}$		14		
$(4.46 \pm 0.29)\ 10^{-12}$		9.6		
$(3.64 \pm 0.17)\ 10^{-12}$		5.5		
$(3.21 \pm 0.30)\ 10^{-12}$		2.8		
$(2.58 \pm 0.28)\ 10^{-12}$		1.5		
$(8.45 \pm 0.25)\ 10^{-12}$	295	1000	E1a	M = Ar, R = n-hexane
$(8.45 \pm 0.24)\ 10^{-12}$		531		
$(7.76 \pm 0.12)\ 10^{-12}$		264		
$(7.36 \pm 0.18)\ 10^{-12}$		133		
$(6.63 \pm 0.26)\ 10^{-12}$		93		
$(6.19 \pm 0.12)\ 10^{-12}$		53		
$(5.20 \pm 0.18)\ 10^{-12}$		27		
$(4.40 \pm 0.33)\ 10^{-12}$		13		
$(3.86 \pm 0.07)\ 10^{-12}$		9.5		
$(2.98 \pm 0.35)\ 10^{-12}$		5.5		
$(2.26 \pm 0.13)\ 10^{-12}$		2.8		
$(1.79 \pm 0.17)\ 10^{-12}$		1.5		
$6.6\ 10^{-12}$	300	$1.05\ 10^3$	F	M = synth. air, R = propane

$k_o/[Air] = (5.9\ ^{+\ 3.0}_{-\ 1.0})\ 10^{-29}\ cm^6 s^{-1}$; $k_\infty = (8.5 \pm 0.6)\ 10^{-12} cm^3 s^{-1}$; $F_c = 0.7$;
$k_o^{air} : k_o^{Ar} : k_o^{He} = 1.6:1:0.5$ /18/

4. 2.2 Propene

$$OH + C_3H_6 \longrightarrow \text{products}$$

$k/cm^3\ s^{-1}$	T/K	p/hPa	Method	Comments
Absolute rate measurements:				
$(1.1 \pm 0.3)\ 10^{-11}$	297	1.3	B	
$(2.3 \pm 0.4)\ 10^{-11}$	298	13.3	B	M = Ar a)
$(3.0 \pm 0.6)\ 10^{-11}$	295	128.1	B	
$(2.2 \pm 0.4)\ 10^{-11}$	295	1013	C	M = synth. air

a) Pressure dependence interpreted in terms of a "fall-off" curve calculated from symmetrical Kassel integrals.
$k_0/[Ar] = (8 \pm 4)\ 10^{-28}$; $k_\infty = (3.0 \pm 0.6)\ 10^{-11}\ cm^3/s$, $F_c = 0.8$ /17/

4. 2.2 (continued)

$k/cm^3\ s^{-1}$	T/K	p/hPa	Method	Comments
Relative measurements:				
$(2.8 \pm 0.3)\ 10^{-11}$	300	1000	E2b	M = synth. air, R = n-hexane
$(2.8 \pm 0.3)\ 10^{-11}$	295	1000	E2a	M = synth. air, R = ethene
$(2.83 \pm 0.22)\ 10^{-11}$	295	998	E1a	M = synth. air, R = n-hexane
$(2.70 \pm 0.11)\ 10^{-11}$		530		
$(2.73 \pm 0.08)\ 10^{-11}$		265		
$(2.91 \pm 0.04)\ 10^{-11}$		93		
$(2.82 \pm 0.08)\ 10^{-11}$		27		
$(2.63 \pm 0.08)\ 10^{-11}$		13.5		
$(2.55 \pm 0.09)\ 10^{-11}$		9.5		
$(2.46 \pm 0.09)\ 10^{-11}$		5.5		
$(2.16 \pm 0.07)\ 10^{-11}$		2.8		
$(1.92 \pm 0.12)\ 10^{-11}$		1.5		
$(2.86 \pm 0.13) 10^{-11}$	295	1006	E1a	R = n-hexane
$(2.84 \pm 0.01)\ 10^{-11}$		530		M = Ar or synth.air
$(2.78 \pm 0.05)\ 10^{-11}$		265		
$(2.80 \pm 0.06)\ 10^{-11}$		133		
$(2.82 \pm 0.05)\ 10^{-11}$		93		
$(2.76 \pm 0.11)\ 10^{-11}$		53		
$(2.74 \pm 0.04)\ 10^{-11}$		27		
$(2.54 \pm 0.04)\ 10^{-11}$		13.5		
$(2.52 \pm 0.11)\ 10^{-11}$		9.5		
$(2.33 \pm 0.17)\ 10^{-11}$		5.5		
$(2.15 \pm 0.11)\ 10^{-11}$		2.8		
$(1.90 \pm 0.34)\ 10^{-11}$		1.5		
$(2.6 \pm 0.25)\ 10^{-11}$	300	1004	G	M = synth. air, R = ethene

$k_o^M / [M] = (8 \pm 4)\ 10^{-27} cm^6 s^{-1}$ (best fitted value, error may be larger); M = Ar, synth.air

$k_\infty = (3.0 \pm 0.2)$ 10-11 $cm^3\ s^{-1}$; $F_c = 0.5$ /18/

4. 2.3 1-butene

$$OH + C_4H_8 \longrightarrow \text{products}$$

$k/cm^3\ s^{-1}$	T/K	p/hPa	Method	Comments
Absolute rate measurements:				
$(3.8 \pm 0.8)\ 10^{-11}$	295	13.3	B	M = He
Relative measurements:				
$(3.0 \pm 0.3)\ 10^{-11}$	295	1000	E1a	M = synth. air, R = ethene
Relative solution data:				

4. 2.4 iso-butene

$$OH + C_4H_8 \longrightarrow \text{products}$$

$k/cm^3\ s^{-1}$	T/K	p/hPa	Method	Comments
Absolute rate measurements:				
$(5.0 \pm 1.0)\ 10^{-11}$	296	13.3	B	M = He
Relative measurements:				
$(5.7 \pm 0.6)\ 10^{-11}$	295	1000	E1a	M = synth. air, R = propene
$(5.3 \pm 0.3)\ 10^{-11}$	300	1004	G	M = synth. air, R = ethene
Relative solution data:				

4. 2.5 1,3-butadiene

$$C_4H_6 + OH \longrightarrow \text{products}$$

$k/cm^3\ s^{-1}$	T/K	p/hPa	Method	Comments
Absolute rate measurements:				
$(6.5 \pm 1.3)\ 10^{-11}$	295	13.3	B	M = He
Relative measurements:				
$(6.1 \pm 0.6)\ 10^{-11}$	295	1000	E1a	M = synth. air, R = propene
$(6.8 \pm 0.8)\ 10^{-11}$	295	1000	E2a	M = synth. air, R = n-propene
Relative solution data:				

4. 2.6 1-pentene

$$OH + C_5H_{10} \longrightarrow \text{products}$$

$k/cm^3\ s^{-1}$	T/K	p/hPa	Method	Comments
Absolute rate measurements:				
Relative measurements:				
$(3.3 \pm 0.3)\ 10^{-11}$	300	1004	G	M = synth. air, R = n-ethene
Relative solution data:				

4.2.7 cyclohexene

$$C_6H_{10} + OH \longrightarrow \text{products}$$

$k/cm^3\ s^{-1}$	T/K	p/hPa	Method	Comments
Absolute rate measurements:				
$(6.7 \pm 1.3)\ 10^{-11}$	297	13.3	B	M = He
Relative measurements:				
$(7.2 \pm 0.8)\ 10^{-11}$	300	1000	E2b	M = synth. air, R = propene
$(6.3 \pm 0.6)\ 10^{-11}$	295	1000	E1a	M = synth. air, R = propene

Relative solution data:

4.2.8 Ethyne

$$OH + C_2H_2 \longrightarrow \text{products}$$

$k/cm^3\ s^{-1}$	T/K	p/hPa	Method	Comments
Absolute rate measurements:				
$(2.2 \pm 0.3) \times 10^{-13}$	295	1055	C	M = synth. air
$(2.2 \pm 0.3) \times 10^{-13}$		995		
$(2.1 \pm 0.3) \times 10^{-13}$		676		
$(1.9 \pm 0.3) \times 10^{-13}$		417		Effective rate constants for the disappearance of OH influenced by the regeneration of OH in secondary reactions with O_2
$(1.8 \pm 0.3) \times 10^{-13}$		281		
$(1.8 \pm 0.3) \times 10^{-13}$		221		
$(1.6 \pm 0.2) \times 10^{-13}$		169		
$(1.7 \pm 0.3) \times 10^{-13}$		160		
$(1.5 \pm 0.2) \times 10^{-13}$		109		
$(1.5 \pm 0.2) \times 10^{-13}$		107		
$(1.3 \pm 0.2) \times 10^{-13}$		53		
$(1.2 \pm 0.2) \times 10^{-13}$		27		
$(1.0 \pm 0.15) \times 10^{-13}$		13		
$(0.8 \pm 0.15) \times 10^{-13}$		3.1		
$(0.6 \pm 0.15) \times 10^{-13}$		2.7		
$(8.0 \pm 1.2) \times 10^{-13}$	295	1053	C	M = Ar
$(7.2 \pm 1.1) \times 10^{-13}$		532		In the analysis of the pressure dependence allowance was made for a bimolecular contribution k_{bi} to the overall rate constant k. The best fit was obtained with the following parameters: $k_{bi} = (0.5 \pm 0.3) \times 10^{-13}\ cm^3 s^{-1}$ $k_0/[Ar] = (2.5 \pm 0.3) \times 10^{-30}\ cm^6 s^{-1}$ $k_\infty = (8.3 \pm 0.8) \times 10^{-13}\ cm^3 s^{-1}$ $F_c = 0.6$
$(6.6 \pm 1.0) \times 10^{-13}$		233		
$(5.7 \pm 0.9) \times 10^{-13}$		107		
$(3.9 \pm 0.6) \times 10^{-13}$		28		
$(3.9 \pm 0.5) \times 10^{-13}$		13		
$(1.7 \pm 0.5) \times 10^{-13}$		2.9		
$(1.5 \pm 0.5) \times 10^{-13}$		2.8		
$(0.9 \pm 0.3) \times 10^{-13}$		0.8		

4.2.8. **Ethyne** (continued)

$k/cm^3\ s^{-1}$	T/K	p/hPa	Method	Comments
Absolute rate measurements:				
$(5.2 \pm 1.0) \times 10^{-13}$	295	103	C	M = He
$(3.9 \pm 0.8) \times 10^{-13}$		52		
$(2.6 \pm 0.5) \times 10^{-13}$		13		
$(1.7 \pm 0.5) \times 10^{-13}$		2.7		
$(7.9 \pm 1.6) \times 10^{-13}$	295	1027	C	M = N_2
$(7.2 \pm 1.4) \times 10^{-13}$		549		
$(5.6 \pm 1.1) \times 10^{-13}$		275		
$(5.7 \pm 1.1) \times 10^{-13}$		140		
4.1 ± 0.8	298	17	D	M = N_2
3.3 ± 0.7		19		
6.1 ± 0.6		61		
7.1 ± 0.7		133		
6.4 ± 0.6		136		
8.3 ± 0.6		1000		
8.1 ± 0.7		1030		
$k_o / [N_2] = 5 \cdot 10^{-30}\ cm^6/s$; $k_\infty = 9 \cdot 10^{-13}\ cm^3/s$;				
Relative measurements:				
$(1.2 \pm 0.2) \times 10^{-12}$	300	986	E 2b	M = synth. air R = propane
8.7×10^{-13}	300	1.05×10^3	F	M = synth. air R = propane

Relative solution data:

4. 3 Oxygenated aliphatic hydrocarbons

4.3.1 Methanol

$$OH + CH_3OH \longrightarrow \text{products}$$

$k/cm^3\ s^{-1}$	T/K	p/hPa	Method	Comments
Absolute rate measurements:				
$(7.7 \pm 0.8) \times 10^{-13}$	296	133	A	M = Ar
$(8.0 \pm 1.6) \times 10^{-13}$	297	13.3	B	M = He
$(9.7 \pm 2.0) \times 10^{-13}$	324	13.3		
$(13.3 \pm 2.7) \times 10^{-13}$	372	13.3		
$(27.4 \pm 3.5) \times 10^{-13}$	420	13.3		
$k(T) = (1.2 \pm 0.3) \times 10^{-11} \exp. \left[-(810 \pm 50)K/T\right] cm^3s^{-1}$				/19/
Relative measurements:				
$(1.0 \pm 0.2) \times 10^{-12}$	295	1000	E 1a	M = synth. air R = ethene
$(1.1\text{-}1.16) \times 10^{-12}$	300	1.05×10^3	F	M = synth. air R = ethene
Relative solution data:				
3.7×10^{-12}	300	-	I	

4. 3.2 Ethanol

$$OH + C_2H_5OH \longrightarrow \text{products}$$

$k/cm^3\ s^{-1}$	T/K	p/hPa	Method	Comments
Absolute rate measurements:				
$(2.9 \pm 0.6) \times 10^{-12}$	296	13.3	B	M = He
Relative measurements:				
$(3.7 \pm 0.4) \times 10^{-12}$	295	1000	E 1a	M = synth. air, R = ethene
$(3.1 \pm 0.5) \times 10^{-12}$	300	1000	E 2b	M = synth. air, R = n-hexane

Relative solution data:

4.3.3 n-Propanol

$$OH + C_3H_7OH \longrightarrow \text{products}$$

$k/cm^3\ s^{-1}$	T/K	p/hPa	Method	Comments
Absolute rate measurements:				
$(4.8 \pm 1.0) \times 10^{-12}$	297	13.3	B	M = He
Relative measurements:				
$(5.4 \pm 0.6) \times 10^{-12}$	295	1000	E 1a	M = synth. air, R = ethene
$(5.9 \pm 0.8) \times 10^{-12}$	300	1000	E 2b	M = synth. air, R = n-hexane
Relative solution data:				

4. 3.4 i-Propanol

$$OH + C_3H_7OH \longrightarrow \text{products}$$

$k/cm^3\ s^{-1}$	T/K	p/hPa	Method	Comments
Absolute rate measurements:				
$(4.1 \pm 0.8) \times 10^{-12}$	294	13.3	B	M = He
Relative measurements:				
$(6.8 \pm 0.7) \times 10^{-12}$	295	1000	E 1a	M = synth. air, R = ethene
5.1×10^{-12}	300	1.05×10^3	F	M = synth. air, R = propane
Relative solution data:				
4.2×10^{-12}	300	-	I	

4. 3.5 n-Butanol

$$C_4H_9OH + OH \longrightarrow \text{products}$$

$k/cm^3\ s^{-1}$	T/K	p/hPa	Method	Comments
Absolute rate measurements:				
Relative measurements:				
$(7.9 \pm 0.8) \times 10^{-12}$	295	1000	E 1a	M = synth. air, R = ethene
$(8.3 \pm 0.9) \times 10^{-12}$	300	1000	E 2b	M = synth. air, R = n-hexane
Relative solution data:				

4.3.6 Glycol

$$OH + C_2H_6O_2 \longrightarrow \text{products}$$

$k/cm^3\ s^{-1}$	T/K	p/hPa	Method	Comments
Absolute rate measurements:				
$(7.7 \pm 1.1) \times 10^{-12}$	295	44-267	A	M = Ar

Relative measurements:

Relative solution data:

4.3.7 Propylenglycol

$$OH + C_3H_6O_2 \longrightarrow \text{products}$$

$k/cm^3\ s^{-1}$	T/K	p/hPa	Method	Comments
Absolute rate measurements:				
$(1.2 \pm 0.1) \times 10^{-11}$	295	35-133	A	M = Ar

Relative measurements:

Relative solution data:

4. 3.8 Diethylenglycol

$$OH + C_4H_{10}O_3 \longrightarrow \text{products}$$

$k/cm^3\ s^{-1}$	T/K	p/hPa	Method	Comments
Absolute rate measurements:				
$(3.3 \pm 0.2) \times 10^{-11}$	295	67-333	A	M = Ar

Relative measurements:

Relative solution data:

4. 3.9 Acetaldehyde

$$OH + CH_3CHO \longrightarrow \text{products}$$

$k/cm^3\ s^{-1}$	T/K	p/hPa	Method	Comments
Absolute rate measurements:				
$(1.6 \pm 0.3) \times 10^{-11}$	300	13.3	B	M = He
$(1.4 \pm 0.3) \times 10^{-11}$	300	127.0		
$(1.6 \pm 0.4) \times 10^{-11}$	328	13.4		
$(1.2 \pm 0.3) \times 10^{-11}$	419	13.3		
$(1.3 \pm 0.3) \times 10^{-11}$	474	13.3		
$(1.1 \pm 0.3) \times 10^{-11}$	518	13.3		
No pressure dependence observed between 13.3-127 hPa of Ar. Slight negative temperature dependence: $k(T) = (7.6 \pm 3.5) \times 10^{-12} \exp (220 \pm 170)/T\ cm^3 s^{-1}$				
Relative measurements:				
Relative solution data:				

4.3.10 Butyraldehyde

$$C_3H_7CHO + OH \longrightarrow \text{products}$$

$k/cm^3\ s^{-1}$	T/K	p/hPa	Method	Comments
Absolute rate measurements:				
Relative measurements:				
$(2.7 \pm 0.2) \times 10^{-12}$	295	1000	E 2c	M = synth. air, R = propene
Relative solution data:				

4. 3.11 Acetone

$$OH + C_3H_6O \longrightarrow \text{products}$$

$k/cm^3\ s^{-1}$	T/K	p/hPa	Method	Comments
Absolute rate measurements:				
$(2.3 \pm 0.3) \times 10^{-13}$	296	13-133	A	M = Ar
$(2.2 \pm 0.4) \times 10^{-13}$	298	13.3	B	M = He
Relative measurements:				
$\leq 2 \times 10^{-13}$	295	1000	E 2c	M = synth. air, R = ethane
Relative solution data:				

4. 3.12 2-Butanone

$$OH + C_4H_8O \longrightarrow \text{products}$$

$k/cm^3\ s^{-1}$	T/K	p/hPa	Method	Comments
Absolute rate measurements:				
$(1.2 \pm 0.2) \times 10^{-12}$	296	33-400	A	M = Ar, He
$(1.4 \pm 0.3) \times 10^{-12}$	297	13.3	B	M = Ar or He M = He
Relative measurements:				
$(2.7 \pm 0.3) \times 10^{-12}$	295	1000	E 1a	M = synth. air, R = ethene
$(2.0 \pm 0.4) \times 10^{-12}$	295	1000	E 2c	M = synth. air, R = ethene
Relative solution data:				

4.3.13 Ethylenoxide

$$OH + C_2H_4O \longrightarrow \text{products}$$

$k/cm^3\ s^{-1}$	T/K	p/hPa	Method	Comments
Absolute rate measurements:				
$(5.0 \pm 1.7) \times 10^{-14}$	296	13-133	A	M = Ar
$(8.0 \pm 1.6) \times 10^{-14}$	296	13.3	B	M = Ar a)
$(1.8 \pm 0.4) \times 10^{-13}$	378	13.3		
$(4.0 \pm 0.8) \times 10^{-13}$	435	13.3		
$(1.6 \pm 0.1) \times 10^{-12}$	501	13.3		
$(2.7 \pm 0.5) \times 10^{-12}$	515	13.3		b)

a) Temperature dependence between 296-435 K represented by an Arrhenius expression
$k = (1.1 \pm 0.4) \times 10^{-11} \exp(-1460/T)\ cm^3/s$

b) Increase of k is stronger than predicted from Arrhenius expression in a). Evidence for curved Arrhenius graph.

Vinoxy (CH_2CHO) has been identified as one of the products of this reaction. Its yield (φ) is strongly increasing with pressure ($\varphi \longrightarrow 1$ for $p \longrightarrow 1013$ hPa) /21/

Relative measurements:

$< 10^{-13}$	300	1.05×10^3	F	M = synth. air, R = propane

Relative solution data:

4. 3.14 Furane

$$C_4H_4O + OH \longrightarrow \text{products}$$

$k/cm^3\ s^{-1}$	T/K	p/hPa	Method	Comments
Absolute rate measurements:				
Relative measurements:				
$(4.3 \pm 0.5) \times 10^{-11}$	295	986	E 3b	M = synth. air R = propane
Relative solution data:				

4.3.15 Ethylacetate

$$OH + C_4H_8O_2 \longrightarrow \text{products}$$

$k/cm^3\ s^{-1}$	T/K	p/hPa	Method	Comments
Absolute rate measurements:				
$(1.6 \pm 0.1) \times 10^{-12}$	295	15-270	A	M = Ar (dynamic method)
$(1.8 \pm 0.2) \times 10^{-12}$	296	67	A	M = Ar (static method)
Relative measurements:				
Relative solution data:				
3.7×10^{-12}	300	-	I	

4.4 Halogenated Aliphatic Hydrocarbons

4.4.1 Chloroform

$$OH + CHCl_3 \longrightarrow \text{products}$$

$k/cm^3\ s^{-1}$	T/K	p/hPa	Method	Comments
Absolute rate measurements:				
$(2.3 \pm 0.5) \times 10^{-13}$	298	13.3	B	M = He
Relative measurements:				
$(2.9 \pm 3.0) \times 10^{-13}$	300	1050	F	R = synth. air, R = toluene
Relative solution data:				

4. 4.2 Dichlormethane

$$OH + CH_2Cl_2 \longrightarrow \text{products}$$

$k/cm^3\ s^{-1}$	T/K	p/hPa	Method	Comments
Absolute rate measurements:				
$(1.5 \pm 0.3) \times 10^{-13}$	295	13.3	B	M = He
Relative measurements:				
Relative solution data:				
1×10^{-13}	300	-	I	

4.4.3 2-Chloroethanol

$$OH + C_2H_5ClO \longrightarrow \text{products}$$

$k/cm^3\ s^{-1}$	T/K	p/hPa	Method	Comments
Absolute rate measurements:				
$(1.4 \pm 0.2) \times 10^{-12}$	295	27-400	A	M = Ar

Relative measurements:

Relative solution data:

4.4.4 Vinylchlorid

$$OH + C_2H_3Cl \longrightarrow \text{products}$$

$k/cm^3\ s^{-1}$	T/K	p/hPa	Method	Comments
Absolute rate measurements:				
Relative measurements:				
$(6.8 \pm 0.2) \times 10^{-12}$	300	1004	G	M = synth. air, R = ethene
Relative solution data:				

4. 4.5 Trichloroethylene

$$OH + C_2HCl_3 \longrightarrow \text{products}$$

$k/cm^3\ s^{-1}$	T/K	p/hPa	Method	Comments
Absolute rate measurements:				
Relative measurements:				
$(2.8\text{-}3.0) \times 10^{-12}$	(295-300)	1.05×10^3	F	M = synth. air, R = toluene
2.1×10^{-12}	300	1004	G	M = synth. air, R = ethene
Relative solution data:				

4. 5 Aromatics

4.5.1 Benzene

$$OH + + C_6H_6 \longrightarrow \text{products}$$

$k/cm^3\ s^{-1}$	T/K	p/hPa	Method	Comments
Absolute rate measurements:				
$(3 \pm 2) \times 10^{-13}$	294	1.3	A	M = Ar
$(5.1 \pm 0.9) \times 10^{-13}$		2.7		
$(6.9 \pm 0.9) \times 10^{-13}$		6.3		
$(8.6 \pm 1.4) \times 10^{-13}$		9.4		
$(9.9 \pm 0.7) \times 10^{-13}$		13.0		
$(10.0 \pm 0.5) \times 10^{-13}$		33		
$(11.4 \pm 0.4) \times 10^{-13}$		67		
$(11.4 \pm 0.7) \times 10^{-13}$		133		
$(13.2 \pm 0.9) \times 10^{-13}$		267		
$(12.2 \pm 2) \times 10^{-13}$		533		
$k_0/[Ar] = 4 \cdot 10^{-29} cm^6 s^{-1}$, $k_\infty = 1.3 \cdot 10^{-12}\ cm^3/s$; $F_c = 0.6$				
$k(T) = 1.1 \times 10^{-11} \exp.(-660\ k/T)\ cm^3/s$ between 273-358 K at p = 133 hPa of Ar.				
$(9.1 \pm 0.4) \times 10^{-13}$	296	33	A	M = He
$(9.5 \pm 0.8) \times 10^{-13}$		67		
$(10.5 \pm 0.4) \times 10^{-13}$		133		
$(9.7 \pm 0.4) \times 10^{-13}$		333		
$(10.2 \pm 0.4) \times 10^{-13}$		667		
$(4.6 \pm 0.8) \times 10^{-13}$	300	1.5	B	M = Ar a)
$(6.0 \pm 1.2) \times 10^{-13}$	295	6.5		
$(8.5 \pm 1.6) \times 10^{-13}$	300	13.3		
$(1.2 \pm 0.2) \times 10^{-12}$	298	41.8		
$(1.1 \pm 0.2) \times 10^{-12}$	295	112.1		
$(7.6 \pm 1.5) \times 10^{-13}$	244	122.4		b)
$(1.3 \pm 0.2) \times 10^{-12}$	366	127.4		
$(8.3 \pm 1.6) \times 10^{-13}$	373	122.6		
$(5.0 \pm 1.0) \times 10^{-13}$	384	126.6		
$(4.0 \pm 0.8) \times 10^{-13}$	453	122.8		
$(4.3 \pm 0.8) \times 10^{-13}$	523	117.6		

a) Reaction is pressure independent above p > 10 Torr.

b) Temperature dependence is complex. Below T = 330 K the data can be represented in Arrhenius form $k = (6.0 \pm 1.8) \times 10^{-12} \exp[-(500 \pm 50\ K/T)]\ cm^3/s$ corresponding to the addition reaction $OH + C_6H_6 \longrightarrow C_6H_6OH$. Between 330-420 K the rate coefficients decrease with increasing temperature. This is attributed to the equilibration of the addition process $OH + C_6H_6 \longrightarrow C_6H_6OH$, which occurs because of the relatively low thermal stability of C_6H_6OH (~ 18 kcal/mol) /8/.

4. 5.1 **Benzene** (continued)

$k/cm^3\ s^{-1}$	T/K	p/hPa	Method	Comments
Absolute rate measurements:				
$(9.7 \pm 0.5) \times 10^{-13}$	296	1030	D	M = N_2, air
Relative measurements:				
1.1×10^{-12} *)	296	933	E1a	M = synth. air, R = n-butane
0.9×10^{-12} *)		408		
$(1.1 \pm 0.1) \times 10^{-12}$		133		
$(1.1 \pm 0.2) \times 10^{-12}$		93		
$(0.9 \pm 0.1) \times 10^{-12}$		67		
$(1.1 \pm 0.1) \times 10^{-12}$		53		
$(0.8 \pm 0.08) \times 10^{-12}$		13		
1.1×10^{-12} *)	296	267	E1a	M = Ar, R = n-butane
$(1.1 \pm 0.2) \times 10^{-12}$		133		
1.1×10^{-12} *)		67		
$(0.9 \pm 0.1) \times 10^{-12}$		53		
$(0.7 \pm 0.05) \times 10^{-12}$		13		
$(0.7 \pm 0.1) \times 10^{-12}$		5.3		
$(0.5 \times 10^{-12}$ *)		2.7		*) single measurements
$k_0 / [M] = (8 \pm 4) \times 10^{-19}\ cm^6 s^{-1}$				
M = air, Ar				
$k_\infty = (1.2 \pm 0.1) \times 10^{-12}\ cm^3 s^{-1}$				
$F_c = 0.4$				
$(1.2 \pm 0.1) \times 10^{-12}$	300	1000	E2b	M = synth. air, R = n-butane
1.2×10^{-12}	(296-305)	1050	F	M = synth. air, R = toluene
$(1.04 \pm 0.13) \times 10^{-12}$	300	1004	G	M = synth. air, R = ethene

4.5.2 Deuterated Benzene

$$OH + C_6D_6 \longrightarrow \text{products}$$

$k/cm^3\ s^{-1}$	T/K	p/hPa	Method	Comments	
Absolute rate measurements:					
$(1.1 \pm 0.2) \times 10^{-12}$	298	114.4	B	M = Ar	
$(1.0 \pm 0.2) \times 10^{-12}$	336	119.4			a)
$(7.6 \pm 1.5) \times 10^{-13}$	380	122.9			
$(4.8 \pm 1.0) \times 10^{-13}$	398	123.7			
$(2.8 \pm 0.5) \times 10^{-13}$	436	123.7			
$(2.5 \pm 0.5) \times 10^{-13}$	524	117.8			

a) Temperature dependence complex as for benzene

Relative measurements:

Relative solution data:

4. 5.3 **Toluene**

$$C_7H_8 + OH \longrightarrow \text{products}$$

$k/cm^3\ s^{-1}$	T/K	p/hPa	Method	Comments
Absolute rate measurements:				
Relative measurements:				
$(6.1 \pm 0.6) \times 10^{-12}$	300	1000	E 2b	M = synth. air, R = benzene
$(5.7 \pm 0.9) \times 10^{-12}$	300	1004	G	M = synth. air, R = ethene
Relative solution data:				
8.4×10^{-12}	300	-	I	

4.5.4 o-Xylene

$$OH + C_7H_{10} \longrightarrow \text{products}$$

$k/cm^3\ s^{-1}$	T/K	p/hPa	Method	Comments
Absolute rate measurements:				
Relative measurements:				
$(12.5 \pm 1.2) \times 10^{-12}$	300	1004	G	M = synth. air, R = ethene
1.3×10^{-11}	300	1050	F	M = synth. air, R = mesitylene
Relative solution data:				

4. 5.5 Naphthalene

$$OH + C_{10}H_8 \longrightarrow \text{products}$$

$k/cm^3\ s^{-1}$	T/K	p/hPa	Method	Comments
Absolute rate measurements:				
$(1.5 \pm 0.4) \times 10^{-11}$	337	128.3	B	M = Ar a)
$(1.1 \pm 0.3) \times 10^{-11}$	358	122.4		
$(7.0 \pm 2.3) \times 10^{-12}$	377	6.6		
$(7.8 \pm 2.1) \times 10^{-12}$	380	13.3		
$(8.3 \pm 3.0) \times 10^{-12}$	380	85.1		
$(10.1 \pm 3.5) \times 10^{-12}$	379	127.4		
$(1.1 \pm 0.4) \times 10^{-11}$	407	124.9		
$(1.0 \pm 0.3) \times 10^{-11}$	428	128.1		
$(6.3 \pm 2.5) \times 10^{-12}$	452	127.9		
$(4.3 \pm 2.0) \times 10^{-12}$	476	127.3		
$(1.4 \pm 0.4) \times 10^{-12}$	502	126.4		
$(1.1 \pm 0.4) \times 10^{-12}$	525	127.9		
$(1.1 \pm 0.5) \times 10^{-12}$	523	42.6		
Relative measurements:				
2×10^{-11}	300	1085 ± 25	F	M = synth. air, R = ethene
Relative solution data:				
1.9×10^{11}	300		I	

a) Reaction rate is slightly dependent on pressure. Temparature dependence is complex.

4.5.6 Diphenyl

$$OH + C_{12}H_{10} \longrightarrow \text{products}$$

$k/cm^3\ s^{-1}$	T/K	p/hPa	Method	Comments
Absolute rate measurements:				
$(5.8 \pm 0.8) \times 10^{-12}$	296	133 333	A	M = Ar
Relative measurements:				
7.4×10^{-12}	299 ± 4	1085 ± 25	F	M = synth. air, R = ethene
Relative solution data:				

4.5.7 Acenaphthene

$$OH + C_{12}H_{10} \longrightarrow \text{products}$$

$k/cm^3\ s^{-1}$	T/K	p/hPa	Method	Comments
Absolute rate measurements:				
Relative measurements:				
5.4×10^{-11}	300	1080 ± 30	F	M = synth. air, R = ethene
Relative solution data:				

4.5.8 Fluorene

$$OH + C_{13}H_{10} \longrightarrow \text{products}$$

$k/cm^3\ s^{-1}$	T/K	p/hPa	Method	Comments
Absolute rate measurements:				
Relative measurements:				
1.2×10^{-11}	300	1080 ± 30	F	M = synth. air, R = ethene
Relative solution data:				

4.5.9 Phenanthrene

$$OH + C_{14}H_{10} \longrightarrow \text{products}$$

$k/cm^3\ s^{-1}$	T/K	p/hPa	Method	Comments
Absolute rate measurements:				
Relative measurements:				
1×10^{-11}	300	1050	F	M = synth. air, R = toluene
Relative solution data:				
1.16×10^{-10}	300	-	I	

4.5.10 p-Xylene

$$OH + C_8H_{10} \longrightarrow \text{products}$$

$k/cm^3\ s^{-1}$	T/K	p/hPa	Method	Comments
Absolute rate measurements:				
Relative measurements:				
1.3×10^{-11}	300	1050	F	M = synth. air, R = mesitylene
Relative solution data:				

4.5.11 Phenol

$$OH + C_6H_6O \longrightarrow \text{products}$$

$k/cm^3\ s^{-1}$	T/K	p/hPa	Method	Comments
Absolute rate measurements:				
$(14.6 \pm 12.5) \times 10^{-12}$	296	5	A	M = He /22/
$(27.8 \pm 4.4) \times 10^{-12}$		43		
$(28.3 \pm 4.9) \times 10^{-12}$		133		
$(26.4 \pm 3.2) \times 10^{-12}$		733		
Relative measurements:				
Relative solution data:				
$> 3 \times 10^{-11}$	300	-	I	

4.5.12 **Aniline**

$$C_6H_5NH_2 + OH \longrightarrow \text{products}$$

$k/cm^3\ s^{-1}$	T/K	p/hPa	Method	Comments
Absolute rate measurements:				
$(113 \pm 39) \times 10^{-12}$	296	19	A	M = He /22/
$(117 \pm 13) \times 10^{-12}$		53		
$(119 \pm 16) \times 10^{-12}$		133		
Relative measurements:				
$(1.1 \pm 0.2) \times 10^{-10}$	300	1000	E 1b	M = synth. air, R = cis-2-butene
Relative solution data:				

4.5.13 **Nitrobenzene**

$$OH + C_6H_5NO_2 \longrightarrow \text{products}$$

$k/cm^3\ s^{-1}$	T/K	p/hPa	Method	Comments
Absolute rate measurements:				
$(1.5 \pm 0.5) \times 10^{-13}$	296	33-240	A	M = He

Relative measurements:

Relative solution data:

4. 5.14 Benzonitrile

$$OH + C_7H_5N \longrightarrow \text{products}$$

$k/cm^3\ s^{-1}$	T/K	p/hPa	Method	Comments
Absolute rate measurements:				
$(3.3 \pm 0.3) \times 10^{-13}$	296	13-813	A	M = He

Relative measurements:

Relative solution data:

4.5.15 **Fluorbenzene**

$$OH + C_6H_5F \longrightarrow \text{products}$$

$k/cm^3\ s^{-1}$	T/K	p/hPa	Method	Comments
Absolute rate measurements:				
$(3.6 \pm 0.4) \times 10^{-13}$	296	9	A	M = Ar
$(4.8 \pm 0.7) \times 10^{-13}$		37		
$(5.4 \pm 0.5) \times 10^{-13}$		133		
$(6.0 \pm 2\ ) \times 10^{-13}$		267		
Relative measurements:				
Relative solution data:				

4. 5.16 Chlorobenzene

$$OH + C_6H_5Cl \longrightarrow \text{products}$$

$k/cm^3\ s^{-1}$	T/K	p/hPa	Method	Comments
Absolute rate measurements:				
$(6.7 \pm 0.5) \times 10^{-13}$	296	133	A	M = Ar
Relative measurements:				
10.7×10^{-12}	300	1004	G	M = synth. air, R = ethene
Relative solution data:				

4. 5.17 Bromobenzene

$$OH + C_6H_5Br \longrightarrow \text{products}$$

$k/cm^3\ s^{-1}$	T/K	p/hPa	Method	Comments
Absolute rate measurements:				
$(7.0 \pm 0.7) \times 10^{-13}$	296	133	A	M = Ar

Relative measurements:

Relative solution data:

4. 5.18 Jodobenzene

$$OH + C_6H_5J \longrightarrow \text{products}$$

$k/cm^3\ s^{-1}$	T/K	p/hPa	Method	Comments
Absolute rate measurements:				
$(6.8 \pm 0.2) \times 10^{-13}$	296	7	A	M = Ar
$(8.6 \pm 0.8) \times 10^{-13}$		40		
$(9.3 \pm 0.5) \times 10^{-13}$		133		
Relative measurements:				
Relative solution data:				

4.5.19 o-Nitrophenol

$$OH + C_6H_5NO_3 \longrightarrow \text{products}$$

$k/cm^3\ s^{-1}$	T/K	p/hPa	Method	Comments
Absolute rate measurements:				
$(9.85 \pm 1.50) \times 10^{-13}$	294	20	A	M = Ar
$(8.27 \pm 1.20) \times 10^{-13}$		70		
$(9.00 \pm 0.70) \times 10^{-13}$		130		
$(9.22 \pm 1.20) \times 10^{-13}$		650		
$(9.0 \pm 2.2) \times 10^{-13}$	313	130		
$(8.2 \pm 1.1) \times 10^{-13}$	334	130	A	$k = (4.2 \pm 0.5) \times 10^{-13} \cdot \exp[+(217 \pm 61)/T)$
$(7.7 \pm 1.1) \times 10^{-13}$	353	130		
Relative measurements:				
Relative solution data:				

4. 5.20 **p-Nitrophenol**

$$OH + C_6H_5NO_3 \longrightarrow \text{products}$$

$k/cm^3\ s^{-1}$	T/K	p/hPa	Method	Comments
Absolute rate measurements:				
Relative measurements:				
Relative solution data:				
8.3×10^{-12}	300		I	

4.5.21 o-Dichlorobenzene

$$OH + C_6H_4Cl_2 \longrightarrow \text{products}$$

$k/cm^3\ s^{-1}$	T/K	p/hPa	Method	Comments
Absolute rate measurements:				
$(4.2 \pm 0.2) \times 10^{-13}$	293	67-267	A	M = Ar
Relative measurements:				
0.4×10^{-12}	300	1000	G	M = synth. air, R = ethene

Relative solution data:

4. 5.22 m-Dichlorobenzene

$$OH + C_6H_4Cl_2 \longrightarrow \text{products}$$

$k/cm^3\ s^{-1}$	T/K	p/hPa	Method	Comments
Absolute rate measurements:				
$(6.7 \pm 4.5) \times 10^{-13}$	294	40	A	M = Ar
$(6.8 \pm 0.2) \times 10^{-13}$		67		
$(7.2 \pm 0.2) \times 10^{-13}$		133		
$(7.0 \pm 0.4) \times 10^{-13}$		267		

Relative measurements:

Relative solution data:

4.5.23 p-Dichlorobenzene

$$OH + C_6H_4Cl_2 \longrightarrow \text{products}$$

$k/cm^3\ s^{-1}$	T/K	p/hPa	Method	Comments
Absolute rate measurements:				
$(3.0 \pm 0.6) \times 10^{-13}$	295	67	A	M = Ar
$(3.2 \pm 0.2) \times 10^{-13}$		133		
3.4×10^{-13}		200		
Relative measurements:				
4.8×10^{-13}	300	1050	F	M = synth. air, R = ethene
Relative solution data:				

4. 5.24 p-Chloroaniline

$$OH + C_6H_6ClN \longrightarrow \text{products}$$

$k/cm^3\ s^{-1}$	T/K	p/hPa	Method	Comments
Absolute rate measurements:				
8.5×10^{-11}	295	53	A	M = Ar
$(8.2 \pm 0.4) \times 10^{-11}$		133		
8.4×10^{-11}		400		
Relative measurements:				
$\approx 4 \times 10^{-11}$	296 ± 5	1050	F	M = synth. air, R = ethene
Relative solution data:				

4. 5.25 1,2,4-Trichlorobenzene

$$OH + C_6H_3Cl_3 \longrightarrow \text{products}$$

$k/cm^3\ s^{-1}$	T/K	p/hPa	Method	Comments
Absolute rate measurements:				
$(4.8 \pm 0.7) \times 10^{-13}$	296	43	A	M = He
$(5.0 \pm 0.8) \times 10^{-13}$		133		
$(4.6 \pm 0.3) \times 10^{-13}$		400		
$(4.4 \pm 0.8) \times 10^{-13}$		800		
$(2.3 \pm 1) \times 10^{-12} \exp(-(429 \pm 125)/T)$			A	M = He
	273-368	133		/22/
Relative measurements:				
6×10^{-13}	300	1050	F	M = synth. air, R = toluene
Relative solution data:				

4.5.26 **1,4-Dichloronaphthalene**

$$OH + C_{10}H_8Cl_2 \longrightarrow \text{products}$$

$k/cm^3\ s^{-1}$	T/K	p/hPa	Method	Comments
Absolute rate measurements:				
Relative measurements:				
$(6 \pm 1) \times 10^{-12}$	300	1050	F	M = synth. air, R = toluene
Relative solution data:				

4. 6 Nitrogen compounds

4.6.1 Hydrogen cyanide

$$OH + HCN \longrightarrow \text{products}$$

$k/cm^3\ s^{-1}$	T/K	p/hPa	Method	Comments
Absolute rate measurements:				
$(3.3 \pm 0.7) \times 10^{-15}$	294	12.5	B	M = He a)

a) Reaction is pressure and temperature dependent /24, 25/

Relative measurements:

Relative solution data:

4. 6.2 **Urea**

$$OH + CH_4N_2O \longrightarrow \text{products}$$

$k/cm^3\ s^{-1}$	T/K	p/hPa	Method	Comments
Absolute rate measurements:				
Relative measurements:				
Relative solution data:				
1.1×10^{-14}	300	-	I	

4. 6.3 Acetonitrile

$$OH + CH_3CN \longrightarrow \text{products}$$

$k/cm^3\ s^{-1}$	T/K	p/hPa	Method	Comments
Absolute rate measurements:				
$(1.75 \pm 0.09) \times 10^{-14}$	296	133	A	M = Ar
$(1.77 \pm 0.16) \times 10^{-14}$	296	200		
$(1.91 \pm 0.14) \times 10^{-14}$	296	400		
$k_0/[Ar] = 2 \times 10^{-32}\ cm^6/s$; $k_\infty (2.1 \pm 0.2) \times 10^{-14}\ cm^3/s$; $F_c = 0.6$				
$(2.3 \pm 0.5) \times 10^{-14}$	295	13.3	B	M = He
$(2.7 \pm 0.5) \times 10^{-14}$	296	73.2		
$(3.1 \pm 0.6) \times 10^{-14}$	347	71.9		
$(4.6 \pm 1.0) \times 10^{-14}$	391	77.8		
$(6.4 \pm 1.3) \times 10^{-14}$	444	74.0		
$(15.8 \pm 3.2) \times 10^{-14}$	520	69.0		
$k\ (T) = \exp\left[(7.8 \pm 0.9) \times 10^{-3} \cdot T - (33.7 \pm 0.4)\right] cm^3 s^{-1}$				
Relative measurements:				
$\leq 1 \times 10^{-13}$	295	1000	E 1a	M = synth. air, R = n-butane
$< 10 \times 10^{-13}$	300	1050	F	M = synth. air, R = propane

Relative solution data:

4.6.4 Acrylonitrile

$$OH + C_3H_3N \longrightarrow \text{products}$$

$k/cm^3\ s^{-1}$	T/K	p/hPa	Method	Comments
Absolute rate measurements:				
$(3.4 \pm 0.5) \times 10^{-12}$	296	30-333	A	M = Ar
Relative measurements:				
$(4.0 \pm 0.4) \times 10^{-12}$	295	1000	E 1a	M = synth. air, R = ethene
Relative solution data:				

4.7 Sulfur compounds

4.7.1 Hydrogen sulfide

$$OH + H_2S \longrightarrow \text{products}$$

$k/cm^3\ s^{-1}$	T/K	p/hPa	Method	Comments
Absolute rate measurements:				
Relative measurements:				
$(5.2 \pm 0.8) \times 10^{-12}$	300	986	E 2b	M = synth. air, R = ethene
Relative solution data:				

4.7.2 Methylmercaptane

$$OH + CH_4S \longrightarrow \text{products}$$

$k/cm^3\ s^{-1}$	T/K	p/hPa	Method	Comments
Absolute rate measurements:				
Relative measurements:				
$(12.6 \pm 3.2) \times 10^{-11}$	300	986	E 2b	M = synth. air, R = propene k-value may be too large because of uncontrolled radical chains
Relative solution data:				

4. 7.3 Dimethyl mercaptane

$$OH + C_2H_6S \longrightarrow \text{products}$$

$k/cm^3\ s^{-1}$	T/K	p/hPa	Method	Comments
Absolute rate measurements:				
Relative measurements:				
$(4.3 \pm 0.9) \times 10^{-11}$	300	986	E 2b	M = synth. air, R = propene k-value may be too large because of uncontrolled radical chains
Relative solution data:				

4. 7.4 Thiophene

$$OH + C_4H_4S \longrightarrow \text{products}$$

$k/cm^3\ s^{-1}$	T/K	p/hPa	Method	Comments
Absolute rate measurements:				
Relative measurements:				
$(9.6 \pm 1.5) \times 10^{-12}$	300	986	E 2b	M = synth. air, R = ethene
Relative solution data:				

4. 7.5 Carbonoxysulfide

$$OH + COS \longrightarrow \text{products}$$

$k/cm^3\ s^{-1}$	T/K	p/hPa	Method	Comments
Absolute rate measurements:				
9×10^{-15}	297	13.3	B	M = He

Relative measurements:

Relative solution data:

4. 7.6 Carbon disulfide

$$OH + CS_2 \longrightarrow \text{products}$$

$k/cm^3\ s^{-1}$	T/K	p/hPa	Method	Comments
Relative measurements:				
$(2.35 \pm 0.16) \times 10^{-12}$	308	933	E1b	M = O_2
$(2.40 \pm 0.22) \times 10^{-12}$		933		M = O_2 (666 hPa)+N_2(267 hPa)
$(2.46 \pm 0.27) \times 10^{-12}$		933		M = O_2 (400 hPa)+N_2(533 hPa)
$(1.88 \pm 0.11) \times 10^{-12}$		933		M = O_2 (267 hPa)+N_2(666 hPa)
$(1.75 \pm 0.17) \times 10^{-12}$		933		M = O_2 (133 hPa)+N_2(800 hPa)
$(1.62 \pm 0.30) \times 10^{-12}$		933		M = O_2 (67 hPa)+N_2(866 hPa)
$(2.10 \pm 0.10) \times 10^{-12}$	293	1066	E1b	M = O_2 (133 hPa)+N_2(933 hPa)
$(1.99 \pm 0.10) \times 10^{-12}$		799		M = O_2 (133 hPa)+N_2(666 hPa)
$(1.80 \pm 0.10) \times 10^{-12}$		666		M = O_2 (133 hPa)+N_2(533 hPa)
$(1.81 \pm 0.10) \times 10^{-12}$		533		M = O_2 (133 hPa)+N_2(400 hPa)
$(1.70 \pm 0.16) \times 10^{-12}$		400		M = O_2 (133 hPa)+N_2(267 hPa)
$(1.68 \pm 0.10) \times 10^{-12}$		300		M = O_2 (133 hPa)+N_2(167 hPa)
$(1.29 \pm 0.15) \times 10^{-12}$		200		M = O_2 (133 hPa)+N_2 67 hPa)
$(1.22 \pm 0.10) \times 10^{-12}$		133		M = O_2
				Products are COS and SO_2 at all reaction conditions with [COS] : [SO_2] = 1:1 and [COS] + [SO_2] ≥ 95 %. R = n-butane in all experiments. Complex dependence of k on total pressure and temperature, k increases in the presence of O_2 /11b/
$(3.81 \pm 0.29) \times 10^{-12}$	293	933	E1b	M = O_2
$(3.50 \pm 0.57) \times 10^{-12}$				M = O_2 (666 hPa)+N_2(267 hPa)
$(3.47 \pm 0.48) \times 10^{-12}$				M = O_2 (400 hPa)+N_2(533 hPa)
$(2.99 \pm 0.35) \times 10^{-12}$				M = O_2 (267 hPa)+N_2(666 hPa)
$(1.93 \pm 0.13) \times 10^{-12}$				M = O_2 (133 hPa)+N_2(800 hPa)
$(1.94 \pm 0.15) \times 10^{-12}$				M = O_2 (107 hPa)+N_2(826 hPa)
$(1.69 \pm 0.16) \times 10^{-12}$				M = O_2 (80 hPa)+$N_2$853 hPa)
$(1.63 \pm 0.19) \times 10^{-12}$				M = O_2 (67 hPa)+N_2(866 hPa)
$(5.49 \pm 0.45) \times 10^{-12}$	278	933	E1b	M = O_2
$(5.39 \pm 0.44) \times 10^{-12}$				M = O_2 (666 hPa)+N_2(267 hPa)
$(5.56 \pm 0.45) \times 10^{-12}$				M = O_2 (400 hPa)+N_2(533 hPa)
$(4.61 \pm 0.34) \times 10^{-12}$				M = O_2 (267 hPa)+N_2(666 hPa)
$(4.01 \pm 0.74) \times 10^{-12}$				M = O_2 (133 hPa)+N_2(800 hPa)
$(3.86 \pm 0.39) \times 10^{-12}$				M = O_2 (107 hPa)+N_2(826 hPa)
$(3.38 \pm 0.32) \times 10^{-12}$				M = O_2 (80 hPa)+N_2(853 hPa)
$(2.87 \pm 0.35) \times 10^{-12}$				M = O_2 (67 hPa)+N_2(866 hPa)

4. 7.6 **Carbon disulfide** (continued)

$k/cm^3\ s^{-1}$	T/K	p/hPa	Method	Comments
Relative measurements:				
$(6.27 \pm 0.51) \times 10^{-12}$	264	933	E1b	M = O_2
$(6.18 \pm 0.54) \times 10^{-12}$				M = O_2 (666 hPa)+N_2(267 hPa)
$(6.02 \pm 0.59) \times 10^{-12}$				M = O_2 (400 hPa)+N_2(533 hPa)
$(5.92 \pm 0.49) \times 10^{-12}$				M = O_2 (267 hPa)+N_2(666 hPa)
$(5.57 \pm 0.45) \times 10^{-12}$				M = O_2 (133 hPa)+N_2(800 hPa)
$(5.36 \pm 0.48) \times 10^{-12}$				M = O_2 (107 hPa)+N_2(826 hPa)
$(5.20 \pm 0.32) \times 10^{-12}$				M = O_2 (80 hPa)+N_2(853 hPa)
$(4.89 \pm 0.23) \times 10^{-12}$				M = O_2 (67 hPa)+N_2(866 hPa)

Relative solution data:

4. 7.7 Sulfur dioxide

$$OH + SO_2 \longrightarrow \text{products}$$

$k/cm^3\ s^{-1}$	T/K	p/hPa	Method	Comments
Absolute rate measurements:				
Relative measurements:				
$(1.1 \pm 0.2) \times 10^{-12}$	300	986	E2b	M = synth. air, R = n-butane
Relative solution data:				

4. 8 Other compounds

4.8.1 Hydrogen

$$OH + H_2 \longrightarrow H_2O + H$$

$k/cm^3\ s^{-1}$	T/K	p/hPa	Method	Comments
Absolute rate measurements:				
$(5.8 \pm 1.0) \times 10^{-15}$	295	1013 ± 15	C	M = synth. air

Relative measurements:

Relative solution data:

4.8.2 Carbon monoxide

$$OH + CO \longrightarrow \text{products}$$

$k/cm^3\ s^{-1}$	T/K	p/hPa	Method	Comments
Absolute rate measurements:				
$(1.38 \pm 0.15) \times 10^{-13}$	299	6.5	D	$M = N_2$,
$(1.67 \pm 0.19) \times 10^{-13}$		30		OH from H_2O_2-
$(1.79 \pm 0.06) \times 10^{-13}$		99		photolysis
$(2.00 \pm 0.13) \times 10^{-13}$		261		at 193 nm
$(2.08 \pm 0.14) \times 10^{-13}$		291		
$(2.21 \pm 0.20) \times 10^{-13}$		743		
$(2.12 \pm 0.25) \times 10^{-13}$		761		
$(2.22 \pm 0.35) \times 10^{-13}$		754		$M = N_2$
$(2.10 \pm 0.20) \times 10^{-13}$		760		OH from H_2O-
				photolysis at 193 nm
$k=(1.65 \pm 0.2) \times 10^{-13} \times (1 + 0.34\ [N_2]/atm)\ cm^3 s^{-1}$				
$(1.59 \pm 0.18) \times 10^{-13}$		16		M = air
$(1.78 \pm 0.10) \times 10^{-13}$		100		OH from H_2O_2-
$(2.14 \pm 0.20) \times 10^{-13}$		312		photolysis at 193 nm
$(2.14 \pm 0.20) \times 10^{-13}$		312		
$(2.59 \pm 0.12) \times 10^{-13}$		761		
$k=(1.63 \pm 0.3) \times 10^{-13} \times (1 + 0.61\ [Air]/atm)\ cm^3 s^{-1}$				

Relative measurements:

Relative solution data:

4.8.3 Phosphine

$$OH + PH_3 \longrightarrow PH_2 + H_2O$$

$k/cm^3\ s^{-1}$	T/K	p/hPa	Method	Comments
Absolute rate measurements:				
$(1.4 \pm 0.3) \times 10^{-11}$	249	13.3	B	M = Ar
$(1.7 \pm 0.3) \times 10^{-11}$	249	13.3		
$(1.3 \pm 0.3) \times 10^{-11}$	256	13.3		
$(1.8 \pm 0.3) \times 10^{-11}$	296	13.3		
$(1.2 \pm 0.3) \times 10^{-11}$	296	13.3		
$(1.3 \pm 0.3) \times 10^{-11}$	296	13.3		
$(1.8 \pm 0.3) \times 10^{-11}$	370	13.3		
$(1.8 \pm 0.3) \times 10^{-11}$	438	13.3		
$k(T)=(2.7 \pm 0.6) \times 10^{-11} \exp.(-155/T)\ cm^3 s^{-1}$ /26/				
Relative measurements:				
Relative solution data:				

4.8.4 Hydrogen peroxide

$$OH + H_2O_2 \longrightarrow H_2O + HO_2$$

$k/cm^3\ s^{-1}$	T/K	p/hPa	Method	Comments
Absolute rate measurements:				
$(1.8 \pm 0.15) \times 10^{-12}$	299	30-1026	D	M = N_2 and air

Relative measurements:

Relative solution data:

4. 8.5 Nitric acid

$$OH + HNO_3 \longrightarrow \text{products}$$

$k/cm^3\ s^{-1}$	T/K	p/hPa	Method	Comments
Absolute rate measurements:				
$(1.8 \pm 0.4) \times 10^{-13}$	250	13.3	B	M = Ar a)
$(1.6 \pm 0.3) \times 10^{-13}$	256	13.3		
$(1.2 \pm 0.2) \times 10^{-13}$	296	9.3		
$(7.5 \pm 1.5) \times 10^{-14}$	338	13.3		
$(6.6 \pm 1.4) \times 10^{-14}$	377	13.3		
$(6.0 \pm 1.1) \times 10^{-14}$	378	13.3		
$(6.1 \pm 1.2) \times 10^{-14}$	435	13.3		
$(5.8 \pm 1.2) \times 10^{-14}$	520	13.3		
$(6.3 \pm 1.3) \times 10^{-14}$	525	13.3		

$k(T) = (1.05 \pm 0.4) \times 10^{-14} \exp(705/T)\ cm^3 s^{-1}$ (T = 250-450 K)

a) reaction rate increases with total pressure

Relative measurements:

Relative solution data:

4. 8.6 Pernitric acid

$$HO_2NO_2 + OH \longrightarrow \text{products}$$

$k/cm^3\ s^{-1}$	T/K	p/hPa	Method	Comments
Absolute rate measurements:				
Relative measurements:				
$(4.1 \pm 1.0) \times 10^{-12}$	295	133	E1a	M = N_2, R = propene. Error limits correspond to estimated total error /27/
Relative solution data:				

5. TROPOSHERIC LIFETIMES OF ENVIRONMENTAL CHEMICALS

One of the primary aim s of this project is to estimate chemical lifetimes of chemicals in the atmosphere. Obviously this quantity in connection with transport parameters (e. g. wind speed and direction, eddy diffusion coefficients etc.) determines the spread of chemicals emitted from ground sources into the atmosphere. In the follwing a brief outline of the physico-chemical basis is given how estimations of chemical lifetimes can be made, and what limitations have to be taken into account.
If a chemical transformation of a substance A (abiotic degradation of A) primarily proceeds through a reaction with OH radicals (1),

(1) $OH + A \rightarrow$ products

the rate expression of the process is given by:

(2) $$- \frac{d\,[A]}{dt} = k_{OH}\,[OH] \cdot [A]$$

In this equation $d\,[A]/dt$ is the loss rate of the substance A and $[A]$ its concentration. Obviously it is determined by the product of the concentration $[OH]$ and $[A]$ and the bimolecular rate coefficient k_{OH}. Assuming steady state conditions for $[OH]$ the chemical lifetime of a substance A, τ_A, is given by

(3) $$\tau_A = (k_{OH}\,[OH])^{-1}$$

When several independent reactions contribute to the loss process of A, each reaction can be represented by a partial lifetime τ_{A_i}. In such case, the total chemical lifetime τ_A is given by equ. (4).

(4) $$\tau_A = \left(\sum_i 1/\tau_{A_i}\right)^{-1}$$

However, as has already been mentioned in the preface, the OH reaction is considered to be the dominant primary loss process, and, therefore to a good approximation determines the lifetime τ_A.

In order to estimate the lifetimes of different chemicals not only the appropriate rate coefficients k_{OH} as listed in the data sheets are

necessary, but also average values of atmospheric OH concentrations. With an approximate value for [OH] of 10^6 cm^{-3} (see below) the range of rate coefficients listed in the data sheets from 5×10^{-11} to 10^{-14} $cm^3 s^{-1}$ corresponds to chemical lifetimes of 5 hours to 3 years, respectively. The relevance of these lifetimes may be seen by comparing them with the characteristic mixing times in the troposphere. Due to the instability of the troposphere time scales for intrahemispheric vertical and horizontal mixing range from 0.1 to 0.2 years. Hence, any chemical with a lifetime comparable to or larger than these values would be expected to be fairly uniformly distributed within the hemispheres. Since the mass exchange across the equator is nearly a factor of 10 slower (characteristic time scale for interhemispheric mixing ~1.2 years) correspondingly longer chemical lifetimes are required for uniform mixing between both hemispheres.

This is experimentally confirmed for example for

CH_4, for which global troposheric measurements (also as a function of altitude) are available /28/. On the other hand, shorter lifetimes preclude global mixing and hence infer regional or local distribution.

Two aspects of eq (3) need further empasis. One of them relates to the variation of k_{OH} within the troposphere and the second to the reliability of the 10^6 cm^{-3} OH level.

i) Due to the relatively strong temperature gradient in the troposphere (average lapse rate = - 6.5°/km) the temperature variation of the rate coefficients for bimolecular reactions with significant avtivation energie (E_i) has to be considered /29/. A similar, altitude dependent correction for k_{OH} is necessary for reactions for which the rate coefficient depends on total density (usually recombination reactions) and / or the O_2 concentration. Realistically, however, both effects are largely outweighted by the uncertainties in the OH concentration

ii) Tropospheric OH is formed mainly as a result of O_3 photolysis near 300 nm

(5) $O_3 + h\nu \quad (\lambda \leq 310 \text{ nm}) \longrightarrow O(^1D) + O_2$

(6) $O(^1D) + H_2O \longrightarrow 2\ OH$

At steady state its formation rate is balanced by chemical consumption.

(7) $OH + B \longrightarrow$ products

where B notably CO, CH_4 and O_3. For the free troposphere and for most pollution situations the CO reaction is dominant, leading to a "chemical" lifetime of OH of 2.5 s (for 100 ppb CO) /29a/. Hence, the actual OH level strongly depends on the actual concentrations of O_3, H_2O and CO. Moreover, due to photolysis term (5) it is predicted to show strong diurnal variations. There is no OH at night and hence essentially no degradation of pollutants.

The question how tropospheric OH can be determined has attracted atmospheric chemists for nearly 10 years. The first information comes from model calculations. Assuming the simple reaction sequence (5) - (7) predicts annual average OH concentrations of 1.5×10^5 cm^{-3} for the free troposphere. This figure, however is increased to 5×10^5 cm^{-3} if the coupling of HO_x with NO_x is taken into account /30/. Regional day time concentrations may even be expected in the order of several 10^6 - 10^7 cm^{-3} /31/.

The accuracy of such predictions can only be tested by in-situ measurements. Early attemps to directly measure OH have proved to be largely unsuccessful. Only a long path absorption technique, developed by Perner et al. /32,33/ has recently provided convincing results. For two locations in Germany average noon-time concentrations of OH on sunny days during the summer of $\sim 1.6 \times 10^6$ cm^{-3} were reported.

It is felt that such measurements need to be performed with still higher detection sensitivity in order to also trace the diurnal variation of OH. Moreover, many more data need to be available to have a more comprehensive picture of the OH variation in time and space. For this reason alternative measuring technique have been developed by Comes et al /34/ and Zellner et al /29a,35/, the latter through the support provided by BMFT within this project.

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